Role of Solid State Diffusion Studies in Materials Selection and Process Design for Development of Low Enrichment U-Mo Metallic Nuclear Fuel Systems

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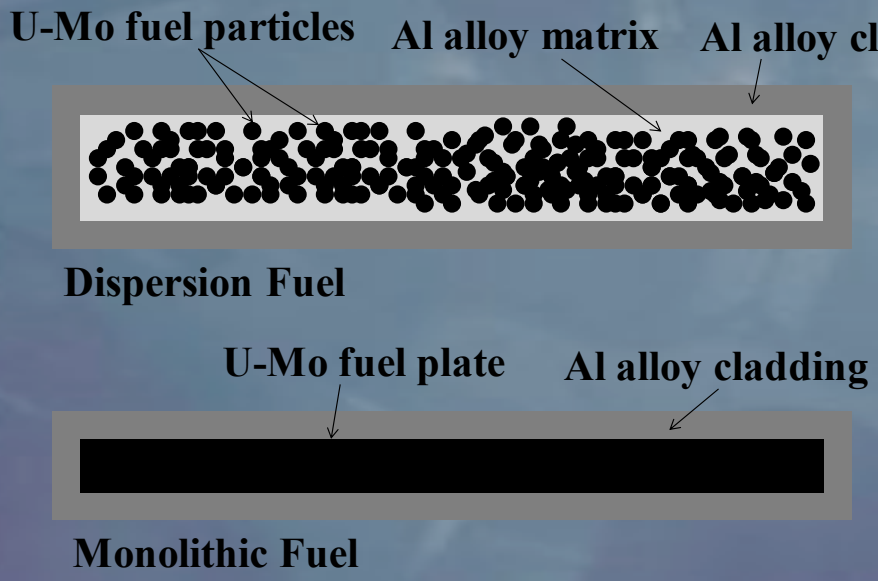
U-Mo Fuel for RERTR/GTRI

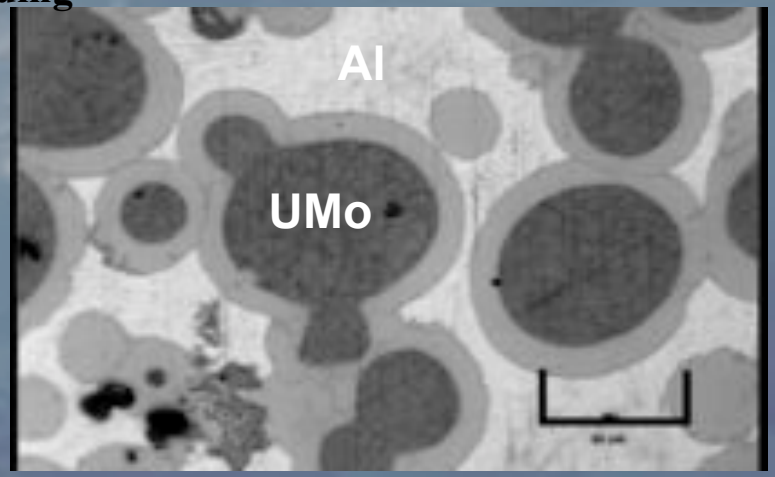
U-Mo Fuel:

- Developed for the program of Reduced Enrichment for Research and Test Reactor (RERTR) – named Global Threat Reduction Initiative (GTRI)
- Dispersed or laminated in aluminum or Al alloy

RERTR/GTRI:

- Convert research and test reactor from using HEU fuels to LEU fuels
- Increase density of U isotopes in the fuel





U-10wt.%Mo vs Al after irradiation**

Fuel-Matrix and Fuel-Cladding Chemical Interaction

Fuel-Matrix and Fuel-Cladding Chemical Interaction (FMCI and FCCI)

- Induced by interdiffusion
- Involves multiple-phases and multiple-components.
- Irradiation enhanced diffusion

Deleterious effects:

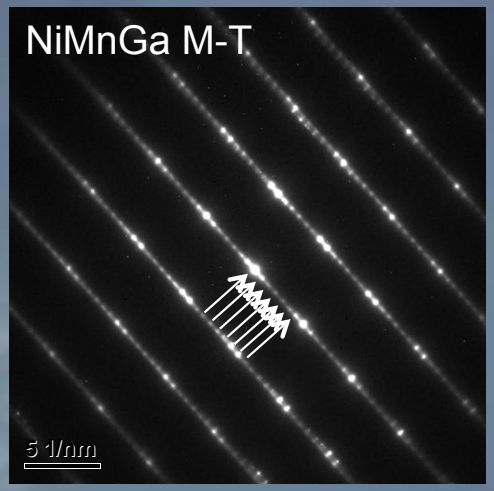
- Thins the cladding layer
- Produces phases with relative low melting point
- Cause cracks due to different thermal expansion coefficients

Engineering Solutions that Require Scientific Understanding:

- Addition of alloying constituents for matrix/cladding
- Placement of barrier layer (or coatings) between metallic fuel and matrix/cladding alloys
- Diffusional interaction between barrier and fuel as well as matrix/cladding alloys

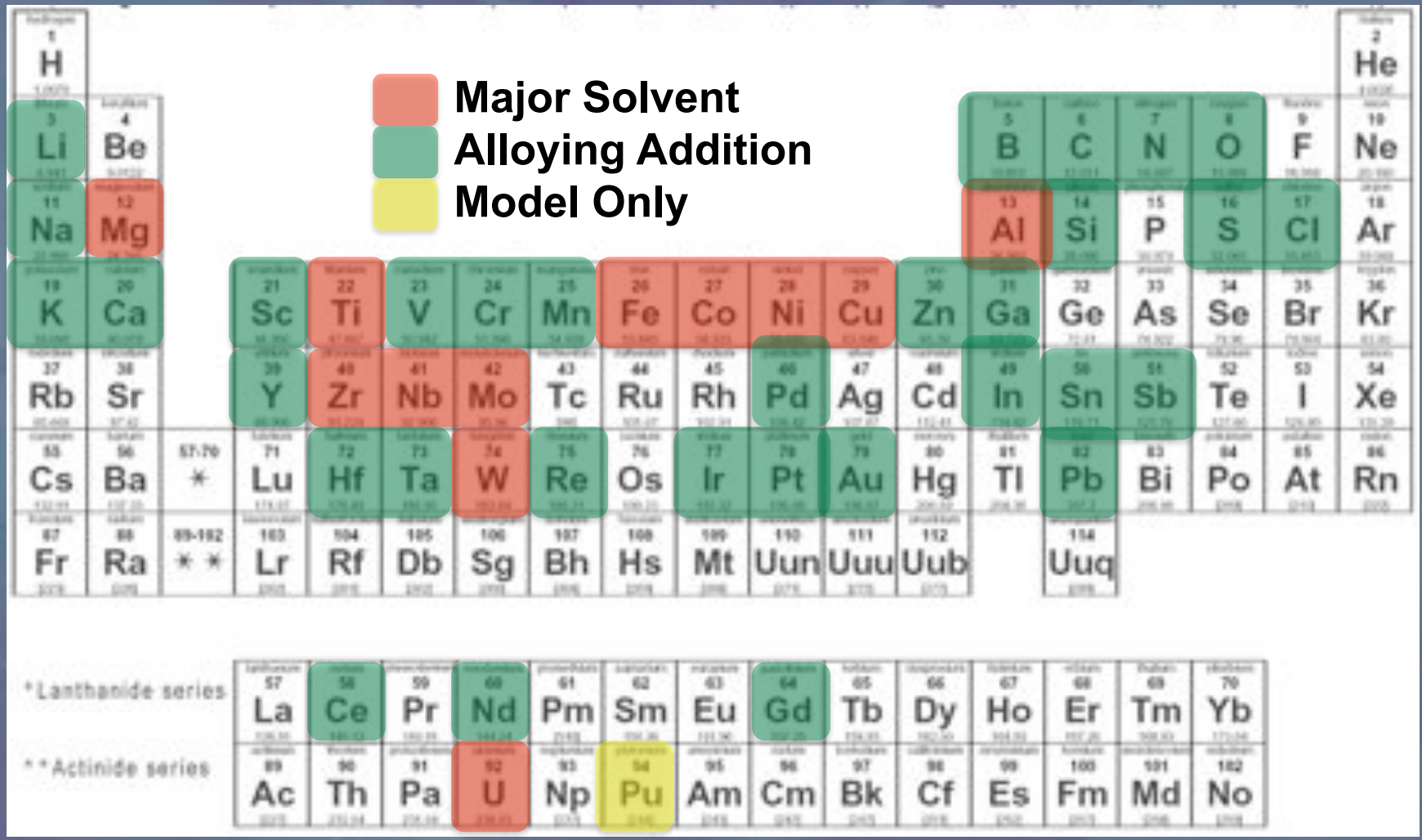
Materials Research at MCEE

- **RERTR/GTRI:**
  - ✓ U-Mo vs. Al Matrix/Cladding Alloys
  - ✓ U-Mo vs. Diffusion Barrier (e.g., Zr, Mo, Nb, Mg)
  - ✓ Zr Barrier vs. Al Cladding Alloys
- **FCRD:**
  - ✓ U-Zr vs. Fe, Fe-Cr, Fe-Cr-Ni Alloys
  - ✓ Fe, Fe-Cr, Fe-Cr-Ni Thin Films on U-Zr
  - ✓ Thermotransport in U-Zr Alloys
- **ATR/NSUF**
  - ✓ Neutron Irradiation of Diffusion Couples with U
- **Diffusion in Mg Alloys for Lightweight**
- **Microstructural Development / Diffusion**
  - ✓ Ni-Mn-Ga and Ni-Mn-In Magnetocaloric Materials
  - ✓ Multiscale (e.g., Nano and Mirco) Al- and Mg-Metal Matrix Composites
  - ✓ Thermal Barrier Coatings for Gas Turbines
  - ✓ High Temperature Heat Transfer Fluid Corrosion



Current Research Activity at MCEE

View by Periodic Chart

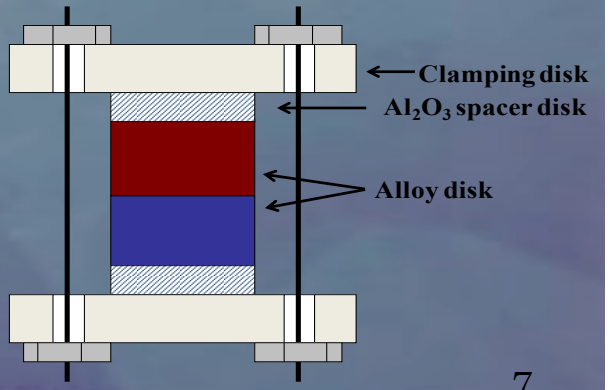


Outline

- **Brief Experimental Details**
- **Diffusion related to U-Mo and Al-alloy matrix/ cladding in dispersion fuels**
- **Diffusion barrier kinetics for Zr, Mo, Nb, and Mg in monolithic fuels**
- **Process design for Zr diffusion barrier:**
  - **Microstructural characterization of HIP fuel plates**
  - **U-Mo-Zr diffusion kinetics and phase equilibria study with quench variation**
  - **Zr interaction with Al-alloy cladding**
- **Summary and future work**

Experimental Details

- Solid-to-solid diffusion couple alloys were cut, polished and assembled under a controlled Ar atmosphere in a glove box.
- Diffusion couples were encapsulated in quartz capsules in Ar atmospheres after Ar flush for heat treatment.
- Diffusion anneal performed using a Lindberg/Blue 3-Zone horizontal tube furnace.
- After anneal the couples were quenched in ice water to preserve the high temperature microstructures.
- The diffusion couples were mounted in epoxy, cross-sectioned and polished for analysis.



Experimental Details

Diffusion Investigations in U-Mo-Al-Si for RERTR Dispersion Fuels

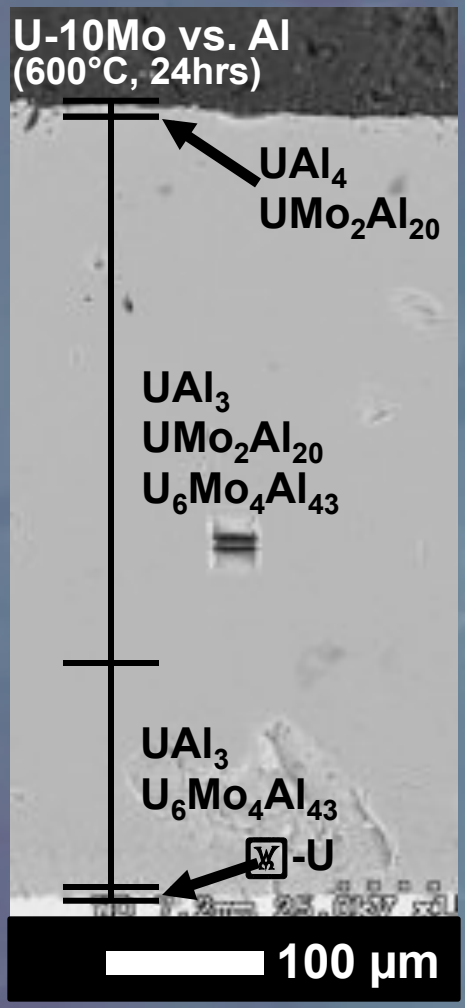
Diffusion Couples:

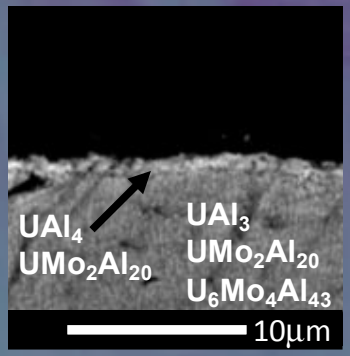
U-Mo vs. Al*
U-Mo vs. Al-Si**
U vs. Mo***

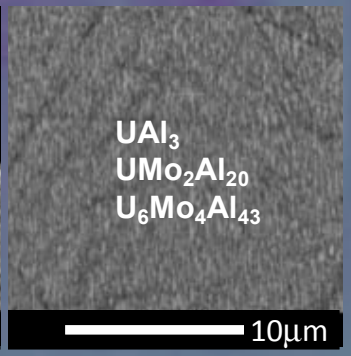
Diffusion Couples (wt.%)	Temperature (°C)	Time (hours)
U 7Mo vs. Al U10Mo vs. Al U12Mo vs. Al	600	24
U 7Mo vs. Al	550	1
U10Mo vs. Al		5
U12Mo vs. Al		20
U 7Mo vs. Al-2Si	550	1
U10Mo vs. Al-2Si		5
U12Mo vs. Al-2Si		20
U 7Mo vs. Al-5Si	550	1
U10Mo vs. Al-5Si		5
U12Mo vs. Al-5Si		20

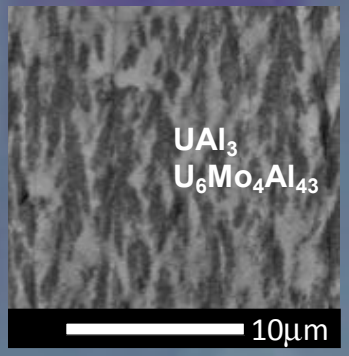
* Perez, et al. Metall. Mater. Trans. A, 2011; 42A: 3071.
** Perez, et al. Metall. Mater. Trans. A, 2013; 44A: 584.
*** K. Huang, et al., Metall. Mater. Trans. A, 2013; 44A: 738.

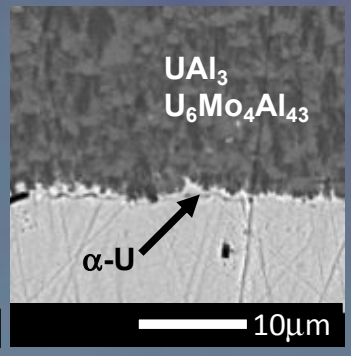
U-Mo vs. Al Diffusion Couples*







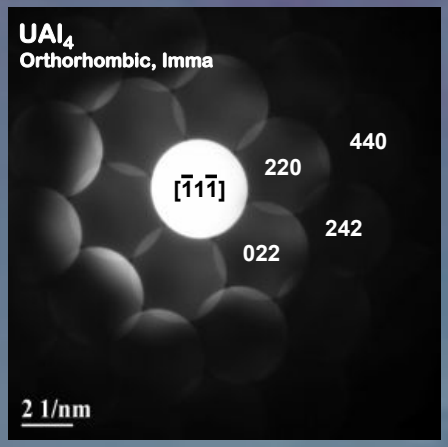


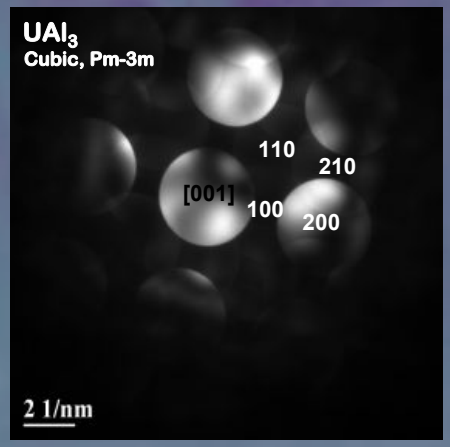


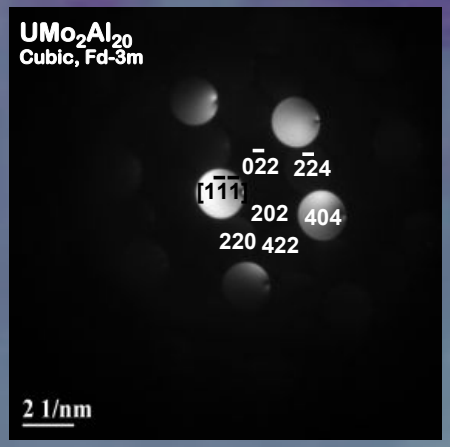
- **Separation of the interdiffusion zone into different phase regions takes place during anneal to produce a stratified structure.**
- **Multi-phase regions composed of various intermetallic phases develop.**
- **Similar microstructures are observed in diffusion couples annealed at 600˚C and 550˚C.**

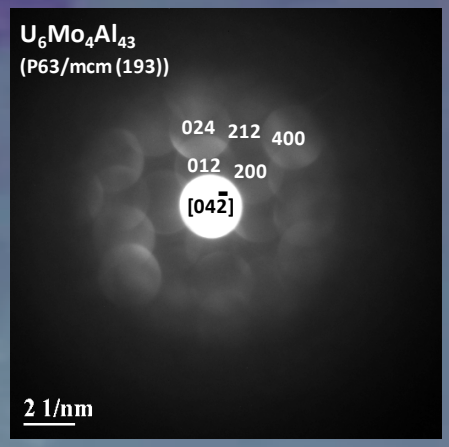
- Perez, et al. Metall. Mater. Trans. A 2011;42:3071.

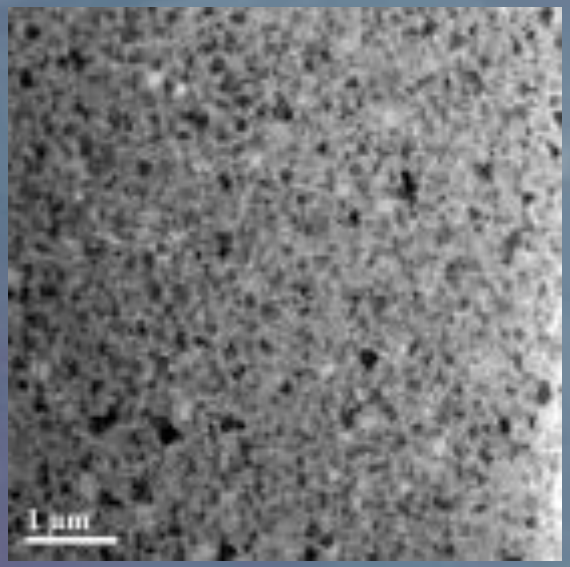
U-Mo vs. Al Diffusion Couples*







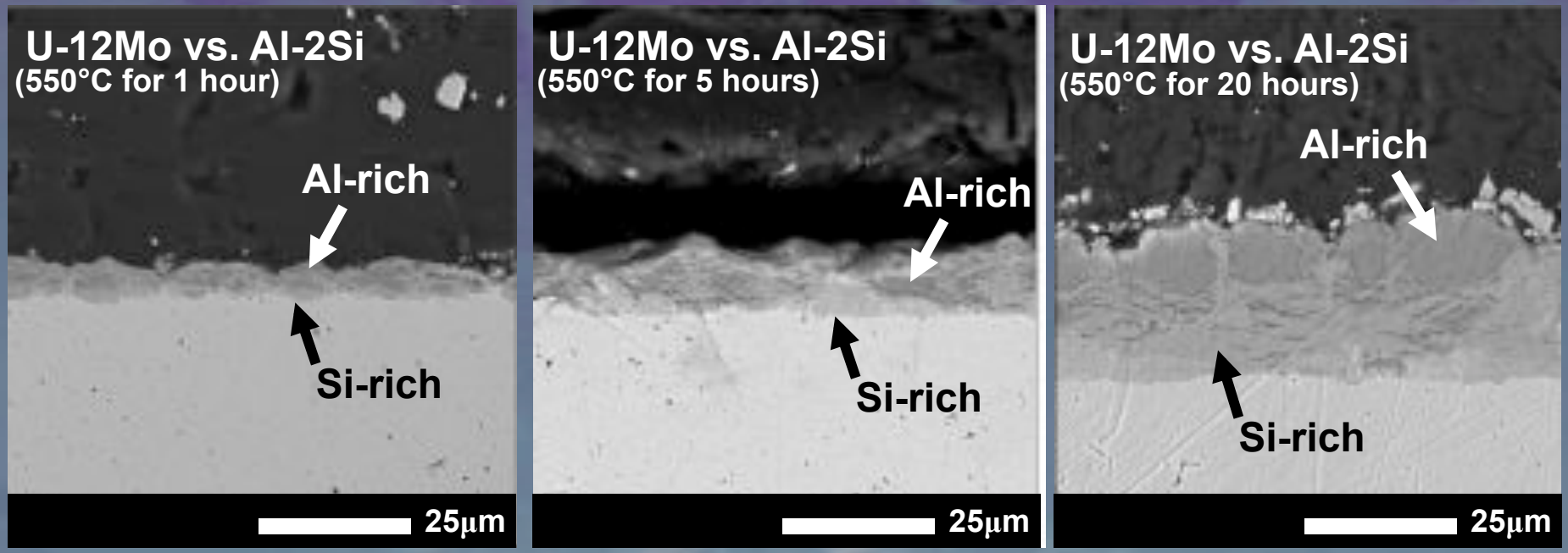




- The interdiffusion zone developed a fine-grained microstructure with grains size less than 1μm.
- Electron diffraction analyses were carried out for selected regions in the interdiffusion zone of the U-10Mo vs. Al diffusion couple annealed at 600˚C for 24 hours.
- The UAl_3, UAl_4, $U_6Mo_4Al_{43}$ and UMo_2Al_{20} phases were identified in the interdiffusion zone in multi-phase layered microstructures.

- Perez, et al. Metall. Mater. Trans. A 2011;42:3071.

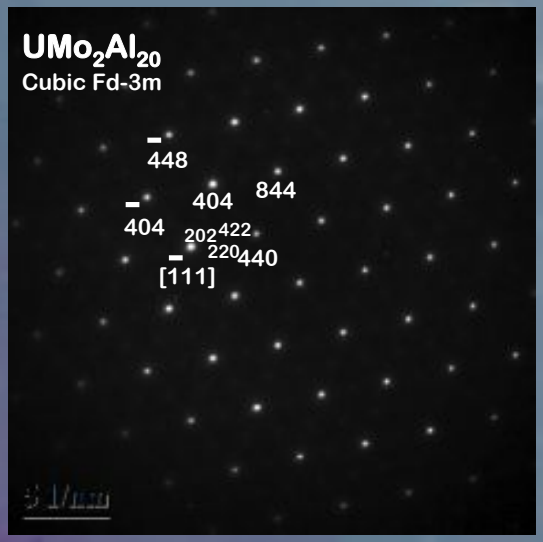
U-Mo vs. Al-Si Diffusion Couples*



- Diffusion couples containing Si in the Al-alloys showed stratification of the interdiffusion zone.
- Complex multi-phase regions developed within 1 hour anneal time.
- Initially discontinuous Al and Si-rich layers develop in the interdiffusion zone.
- After longer diffusion anneal, the observed Si-rich regions grow and develop into continuous layers.

* Perez, et al. Metall. Mater. Trans. A, 2013; 44A: 584.

U-Mo vs. Al-Si Diffusion Couples*



- The $(U,Mo)(Al,Si)_3$ and UMo_2Al_{20} phases were positively identified.
- The $(U,Mo)(Al,Si)_3$ appears to be distributed through the interdiffusion zone with variation in compositions.
  - This phase shows promising results during irradiation and is considered a favored phase.
- More importantly, the UAl_4 and $U_6Mo_4Al_{43}$ phases do "not" develop.
  - The $U_6Mo_4Al_{43}$ potentially behaves poorly with void formation during irradiation.**

**J. Gan, D.D. Keiser, Jr., JNM, 396 (2010) 234.

* Perez, et al. Metall. Mater. Trans. A, 2013; 44A: 584.

U-Mo vs. Al-Si Diffusion Couples: Growth Constants

The growth constant for the interdiffusion zone (i.e., intermetallic phases), assuming simple parabolic growth, was calculated:

$$K = \frac{T}{t^{1/2}}$$

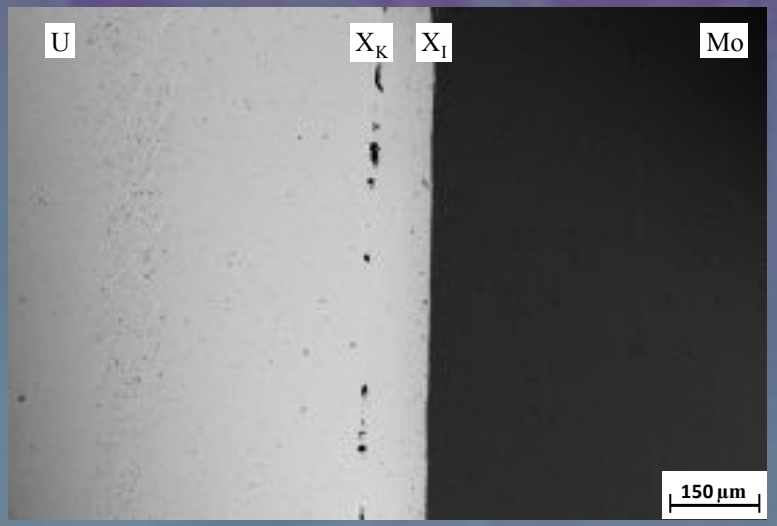
T **is the IDZ thickness and** ***t*** **is the anneal time.**

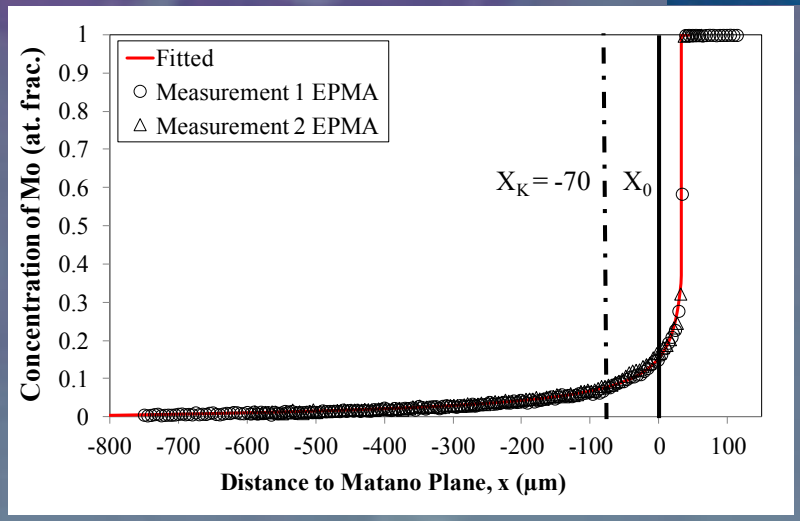
Diffusion Couples	Growth Constant, K ($\mu m/sec^{1/2}$)
U-Mo vs. Al (600˚C)	0.9 - 1.8
U-Mo vs. Al (550˚C)	0.4 - 0.7
U-Mo vs. Al-2Si (550˚C)	0.1 - 0.2
U-Mo vs. Al-5Si (550˚C)	0.1 – 0.2

- **Alloying Al with Si alters the phase constituents (no UAl_4 and $U_6Mo_4Al_{43}$) and decreases the growth kinetics.**

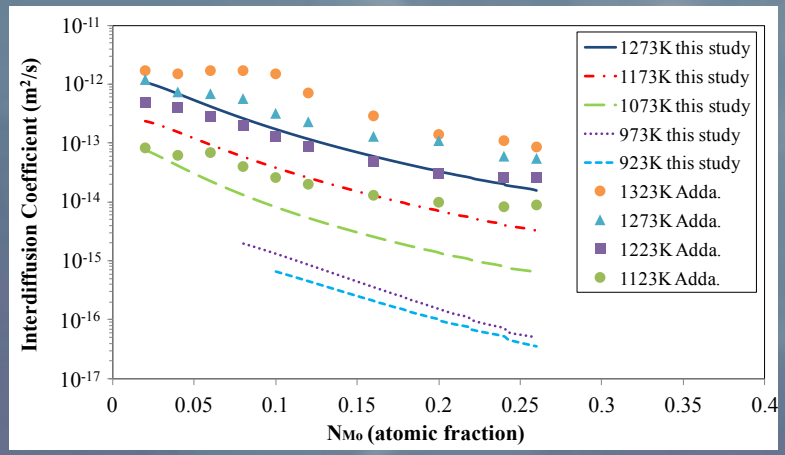
** Perez, et al. Metall. Mater. Trans. A, 2013; 44A: 584.

Diffusion Database

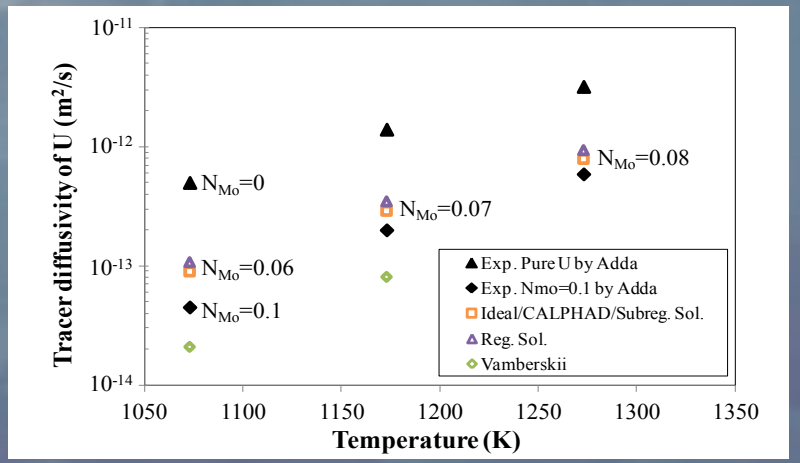




BSE micrograph and concentration profile from the U vs. Mo couple annealed at 1273K for 24 hours.



Interdiffusion Coefficient



Tracer Diffusion Coefficients

K. Huang, et al., Metall. Mater. Trans. A, 2013; 44A: 738.

Diffusion Investigations in U-Mo for RERTR Monolithic Fuels

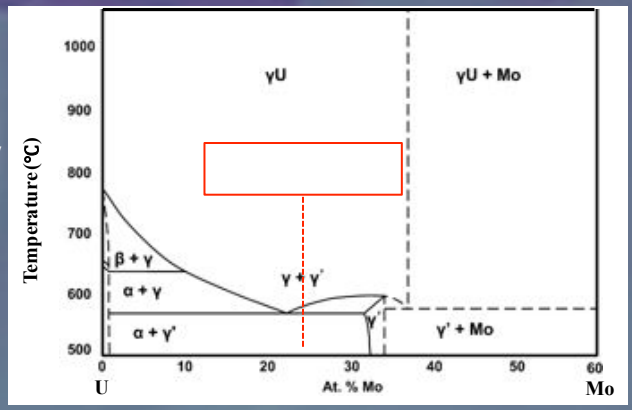
Diffusion Couples:

U-10Mo vs. Zr*
U-10Mo vs. Mo**
U-10Mo vs. Nb***
U-10Mo vs. Mg***

Diffusion Couples	Temperature (°C)	Time (hours)
U10Mo vs. Mo	1000	96
	900	240
	800	480
	700	720
	600	960
U-10Mo vs. Zr	1000	96
	900	240
	800	480
	700	720
	600	960
U-10Mo vs. Nb	1000	96
	900	240
	800	480
	700	720
	600	960
U-7Mo vs. Mg	550	96

* Huang et al., JPED, 2012; 33: 443.
** Huang, et al., JPED, 2013; 34: 307.
*** Huang, et al., JPED, 2014; 35: 146.
**** Huang et al., DDF, 2013; 333: 199.

Barrier Materials Candidates



Refractory element Zr, Mo and Nb*:

- Diffusion of U is slow.
- High melting points and thermal conductivity
- Corrosion resistant is good.

Mo:

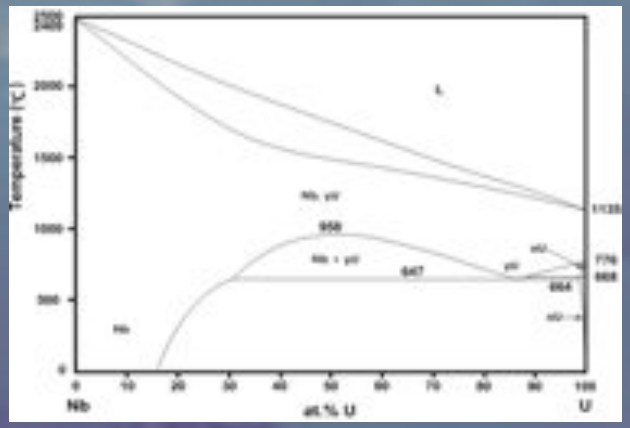
- Maintain the system to be simple binary.
- One intermetallic phase forms between U-Mo and Mo.
- Largest variation in the composition of U-10wt.%Mo fuel can be less than 15 at.% Mo.

Zr:

- Neutrons adsorption rate is one of the lowest among natural metal [4].
- Compatible with current hot rolling process adopted by Idaho National Lab (INL)**.

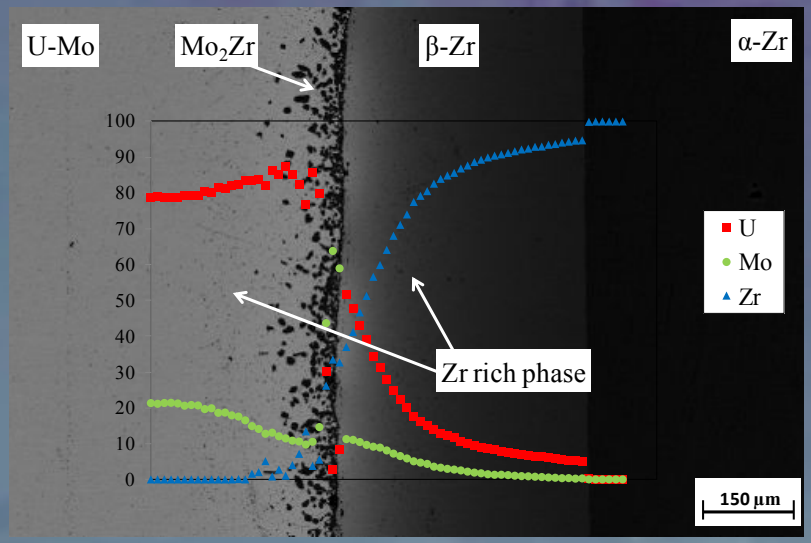
Nb:

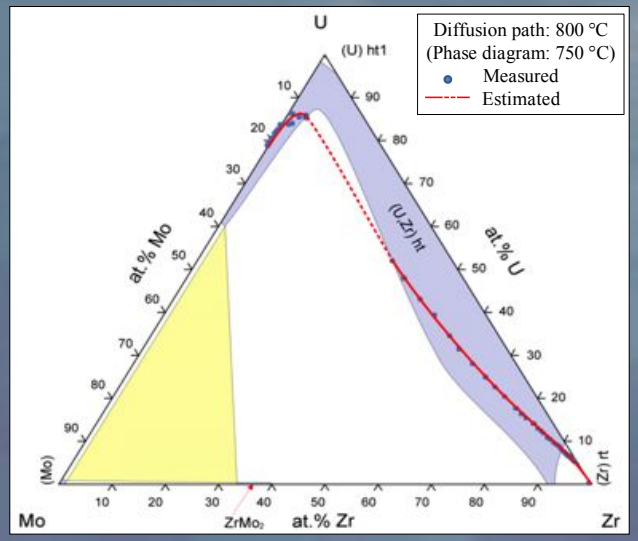
- Forms complete solid solution with U
- Forms less number of intermetallic phases with Al compared to Zr and Mo.



*Davis Jr, et al. ASM Handbook 1992.
**Perez, et al. J Nucl Mater 2010;402:8

Diffusion Microstructure and Diffusion Paths: U-Mo vs. Zr

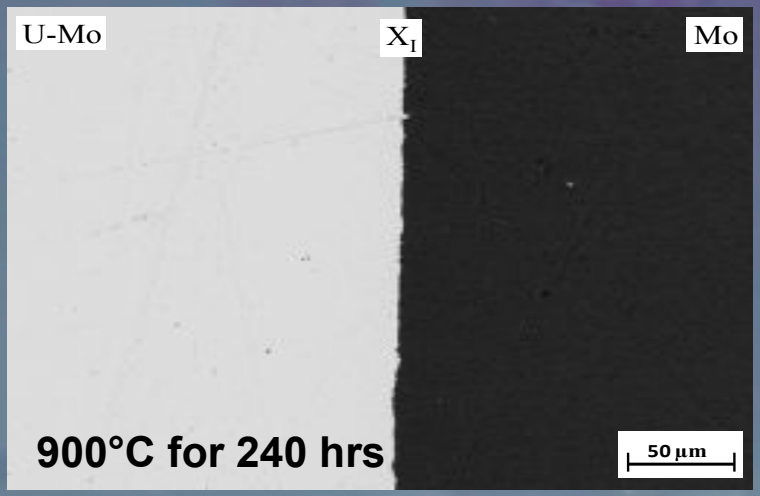


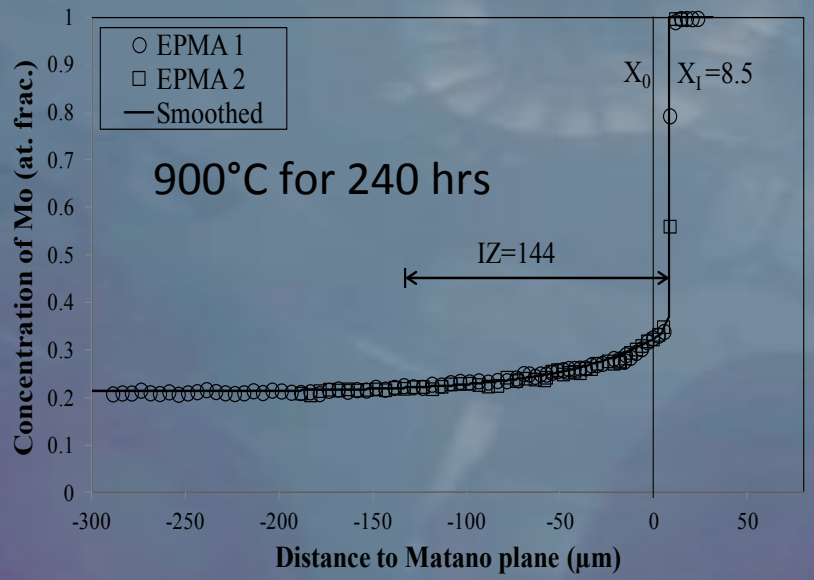


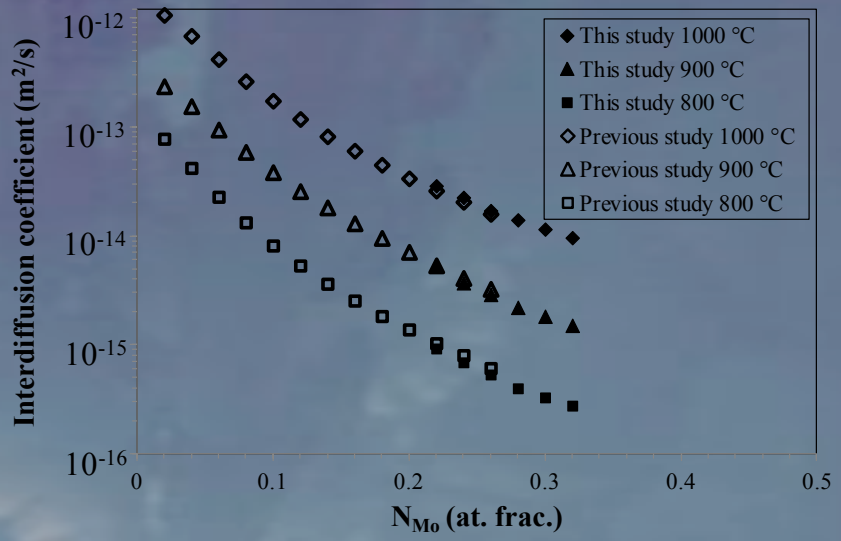
800^{0}C 480 hours

- Boned well at 1000 -600^{0}C.
- γ-U, Mo_2Zr, Zr rich, two phases region, pure Zr were observed.
- Mo_2Zr gets denser when anneal temperature decreased according to the phase diagrams.
- Uphill diffusion of U.
- The estimated diffusion paths agree well with the ternary phase diagram.
- Mo plays a significant role on the diffusion path especially at 700°C.
- About 10^4-10^2 times slower than those between U-10wt.%Mo vs. Al and Al-Si, respectively.

Diffusion Microstructure and Diffusion Paths: U-Mo vs. Mo

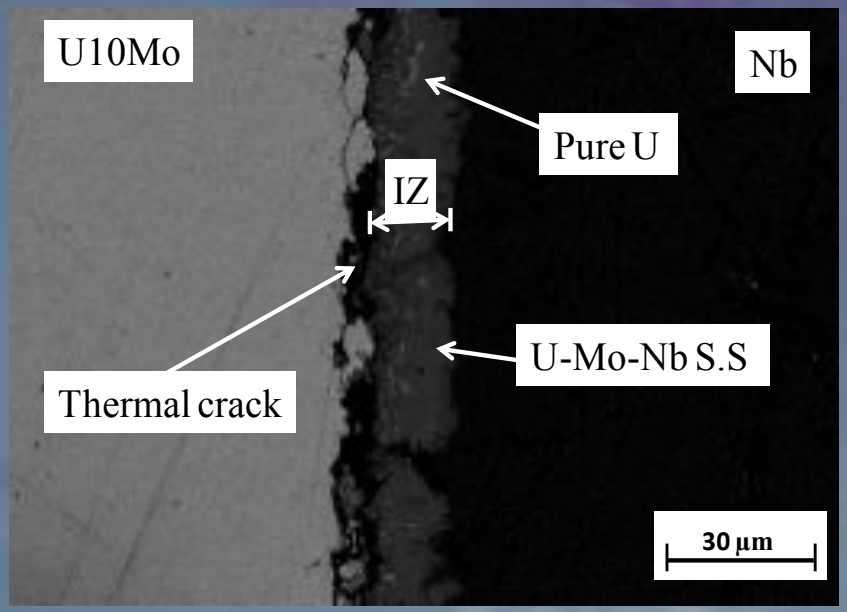




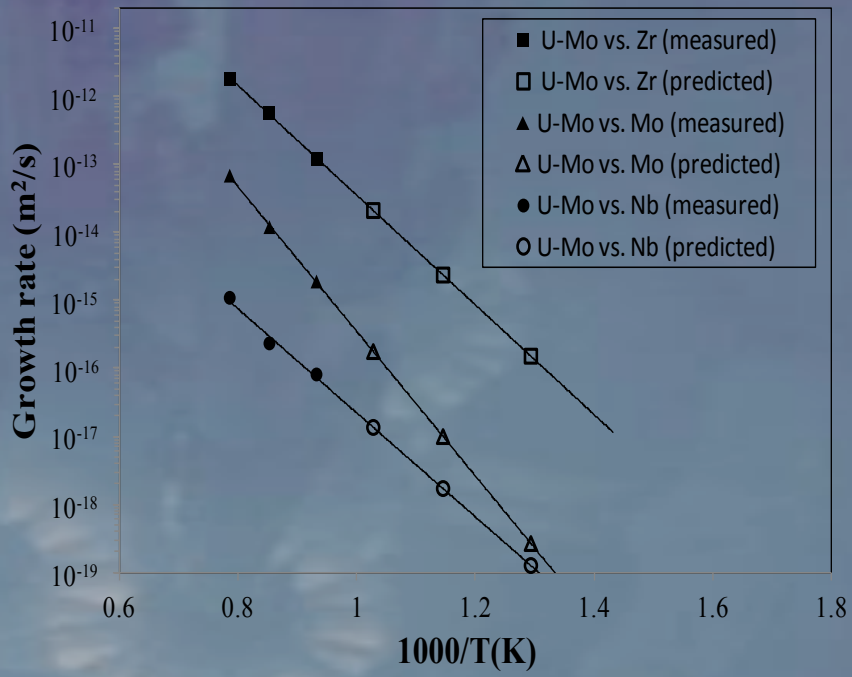


- Boned well at 1000 -600°C.
- No intermetallics formation.
- Atomic mobility and vacancy wind parameters determined for U-Mo solid solution.
- More than 10^5 times slower than those between U-10wt.%Mo vs. Al and Al-Si, respectively.

Diffusion Microstructure and Diffusion Paths: U-Mo vs. Nb



800°C 480 hours



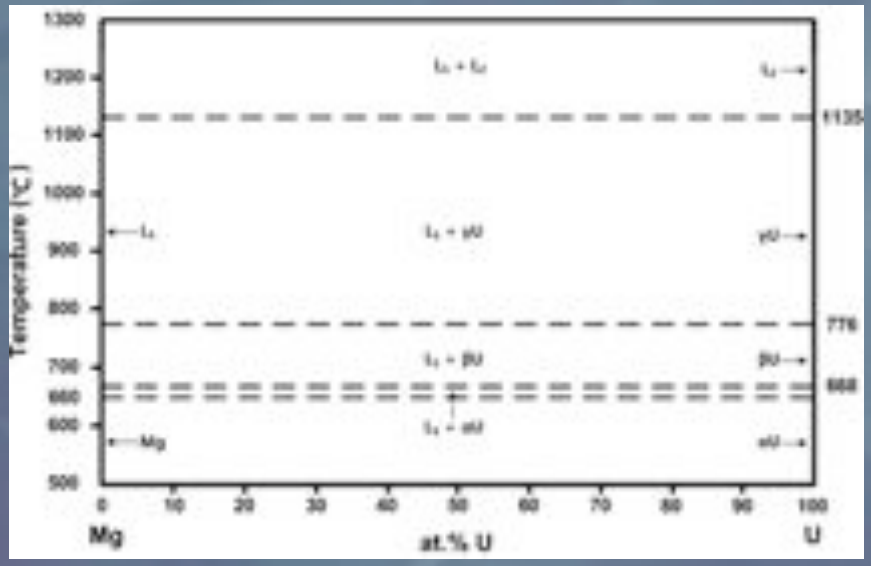
- Intermetallic formation and growth.
- Significant quench cracks after all temperatures of anneal.
- More than 10^6 times slower than those between U-10wt.%Mo vs. Al and Al-Si, respectively.

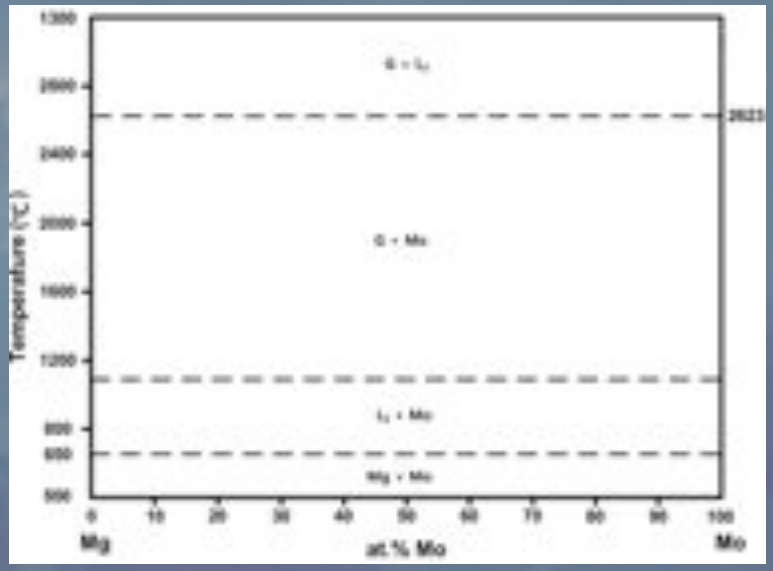
The growth rate of interdiffusion zone between U-10Mo with Zr, Mo, Nb is about 10^4, 10^5 and 10^6 times slower than those in diffusion couples of U-10Mo vs. Al or Al-Si, respectively.

Barrier Materials Candidates

Mg:

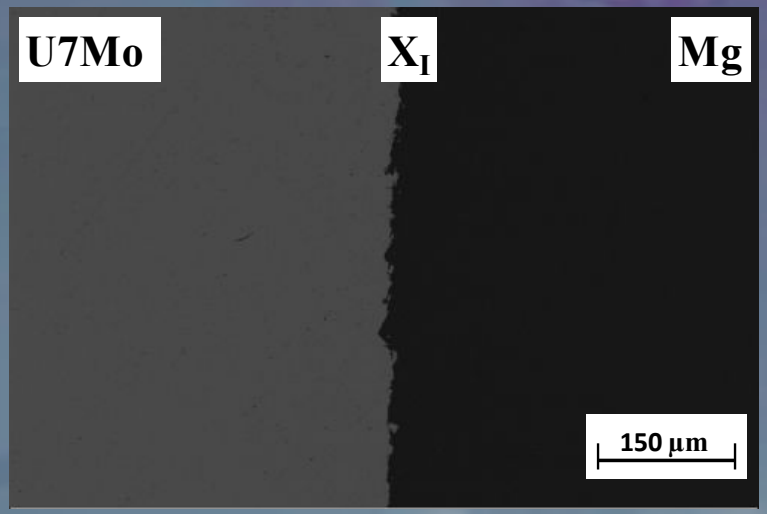
- There is no reactions between Mg with U or Mo based on binary phase diagram.
- Reaction between Mg and Al alloy is insignificant during improved hot rolling process at 275°C reported*.
- The neutron absorption rate of Mg is one of the lowest among natural metal**.
- Thermal conductivity is high, 156 $W \cdot m^{-1} \cdot K^{-1}$.



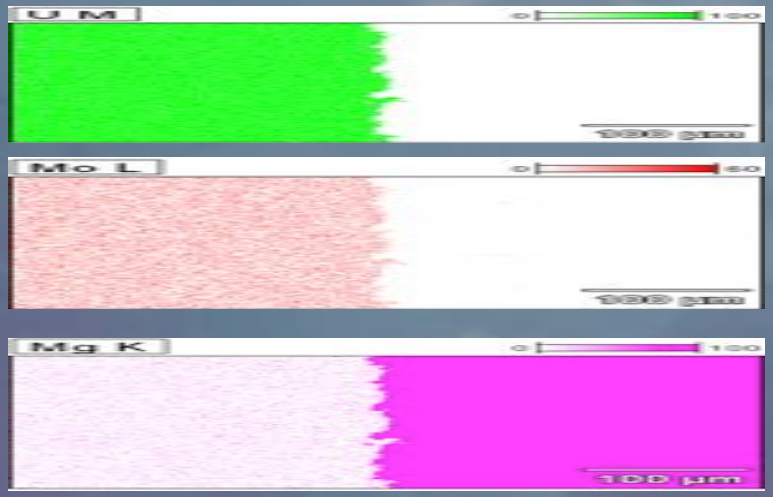


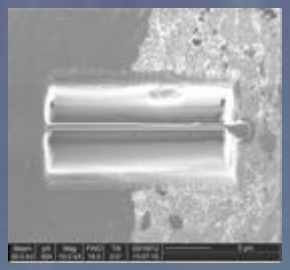
*Wiencek TC, et al. 1998 International Meeting on RERTR. São Paulo, Brazil, 1998.
**Davis Jr, et al. ASM Handbook 1992.

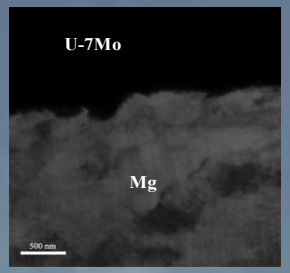
Diffusion Microstructure and Diffusion Paths: U-Mo vs. Mg

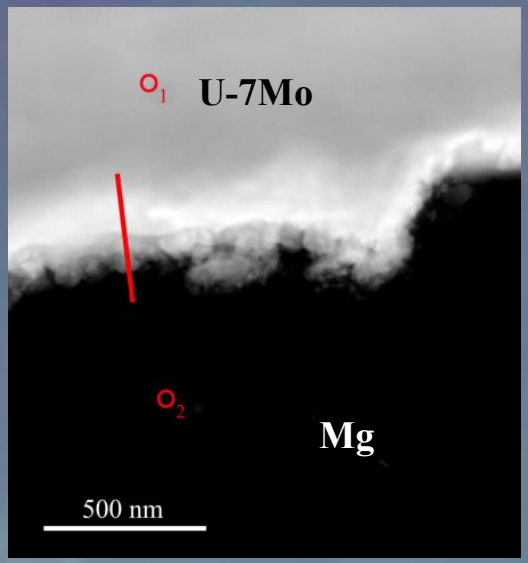


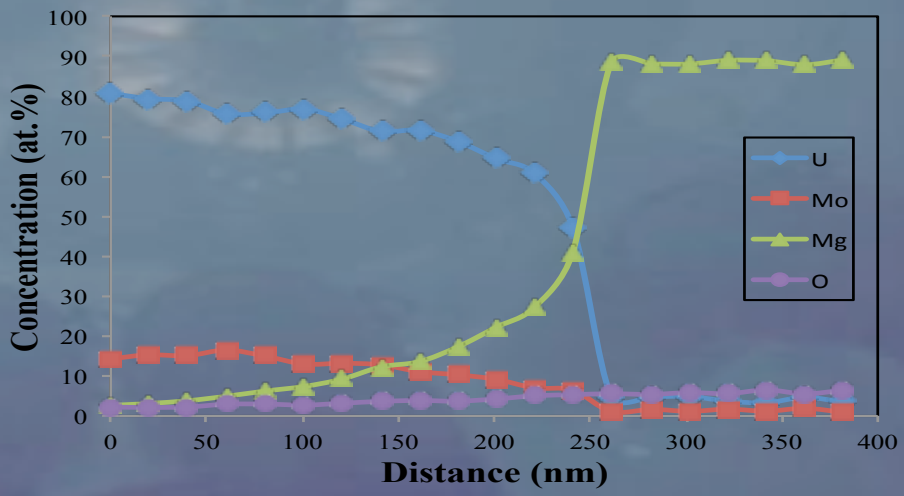
560°C 96 hours











Zr Diffusion Barrier

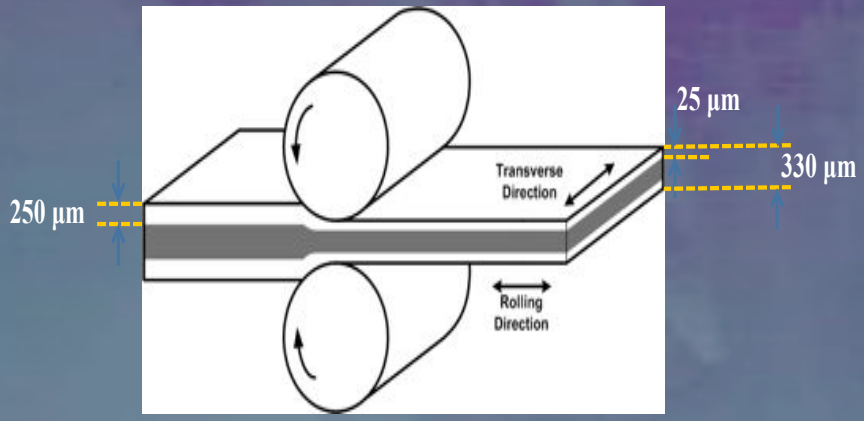
Rolled, HIP'ed and Annealed Fuel Assembly*

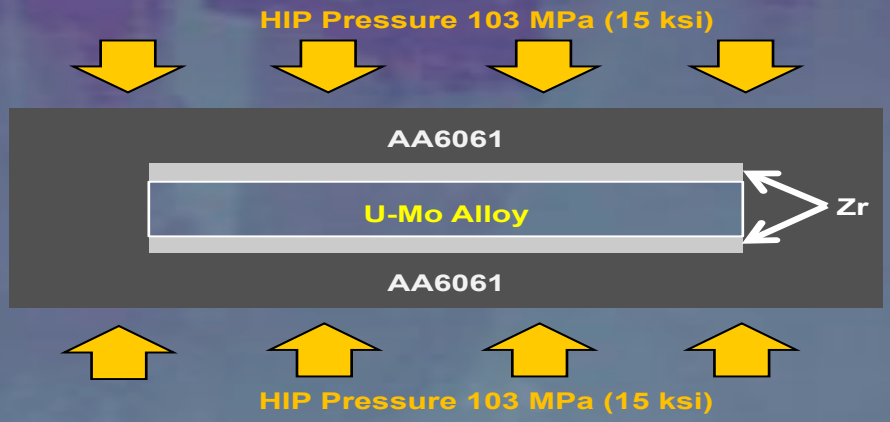
U-Mo-Zr Diffusion Kinetics and Phase Equilibria**

Zr vs. Al-Alloy Cladding***

*Y. Park et al., *Journal of Nuclear Materials*, 2014; 447: 215.
**Y. Park et al., and N. Eriksson et al., Unpublished.
***J. Dickson et al., *Intermetallics*, 2014; 49: 154.
***A. Paz y Puente, et al., *J. Ref. Met. Hard Mater.*, 2014; 43: 317.

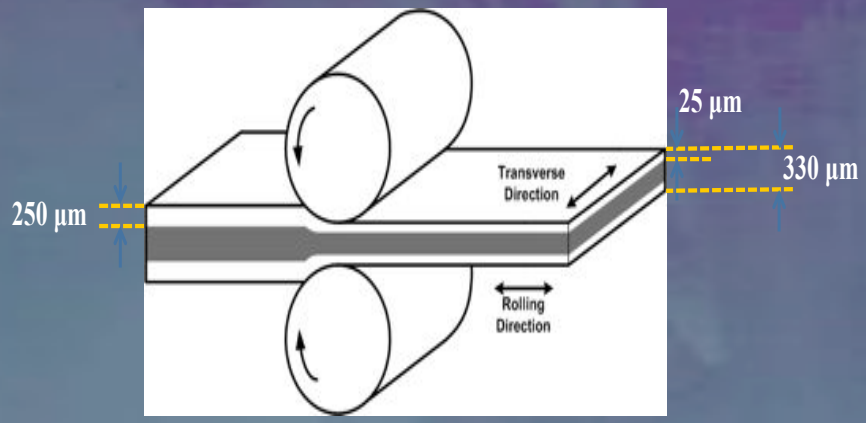
Rolled, HIP'ed and Annealed Fuel Assembly

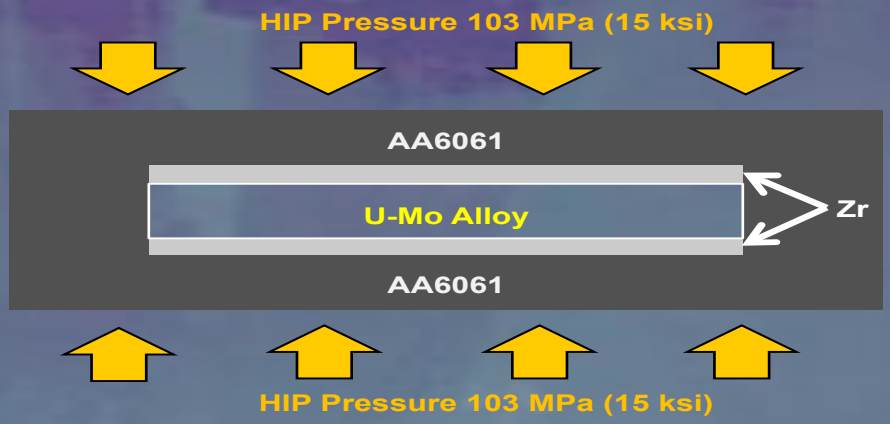




- U-Mo alloy by arc-melting.
- Acid cleaned and laminated, in a carbon steel can, using pure Zr (99.9% pure) foil with a starting thickness of 250 µm.
- The Zr-laminated U-Mo coupon: pre-heated at 650°C for 30 minutes in a furnace, and co-rolled 15 times. A post-rolling annealing treatment was performed at 650°C for 45 minutes.
- Each laminated foil was polished and stacked with AA6061 cladding.
- HIP'ed at various temperatures (520, 540, 560 and 580°C) and durations (45, 60, 90 180 and 345 minutes)
- The HIP heated to the target temperature with a ramp-up and cool-down rate of 280°C per hour with constant pressure at 103 MPa (~15 ksi) using argon pressurizing medium.

Rolled, HIP'ed and Annealed Fuel Assembly





Can we employ higher HIP temperature and longer HIP duration?

Improved adhesion strength, but want to avoid excessive diffusional interactions.

Diffusion Barrier: Zr

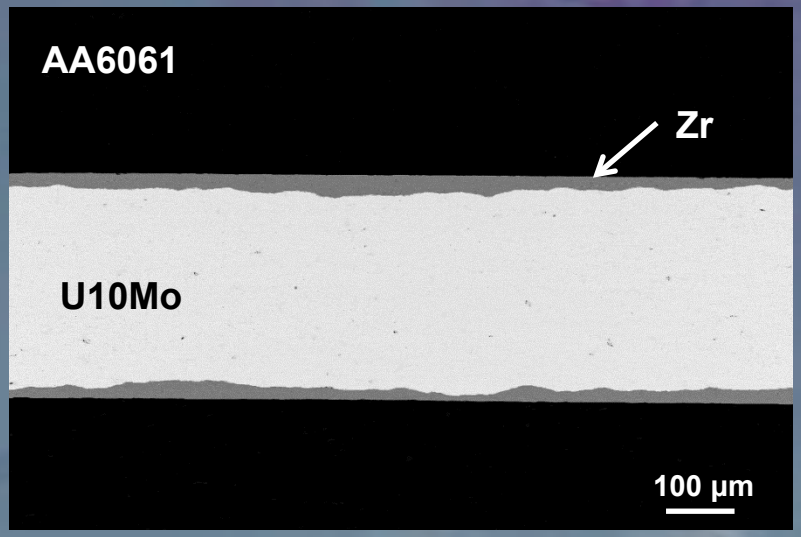
Rolled, HIP'ed and Annealed Fuel Assembly

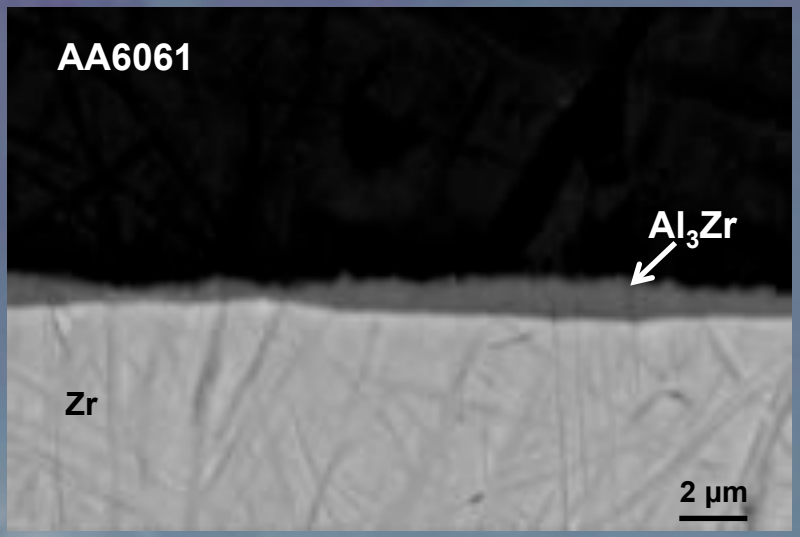
HIP Run	Sample	Temperature (˚C)	Hold Time (minute)	Pressure (ksi)
81[a]	81-4	560	90	15
82	82-5	580	90	15
83	83-5	540	90	15
84	84-4	520	90	15
85	85-5	560	180	15
86	86-5	560	45	15
87	87-5	560	345	15
88	88-5, 88-2[b]	560	60	15
N/A	Alloy 402-2	650	90	

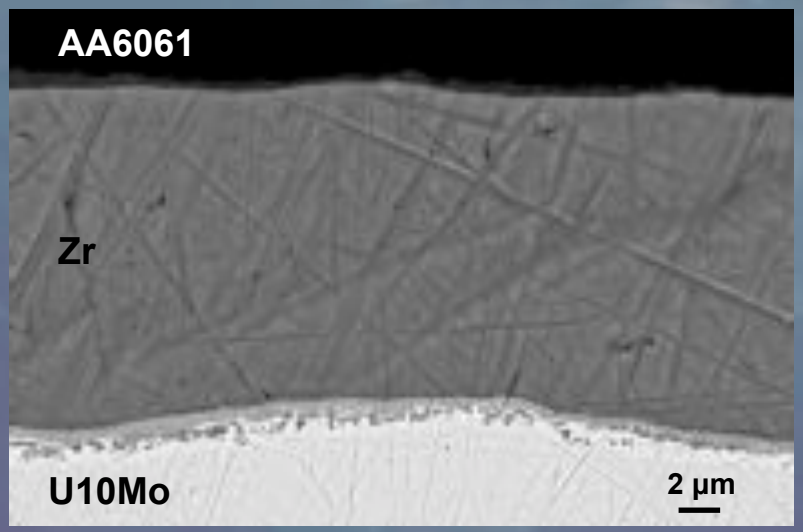
U-Mo/Zr/6061 foils co-rolled at 650˚C for 90 minutes.

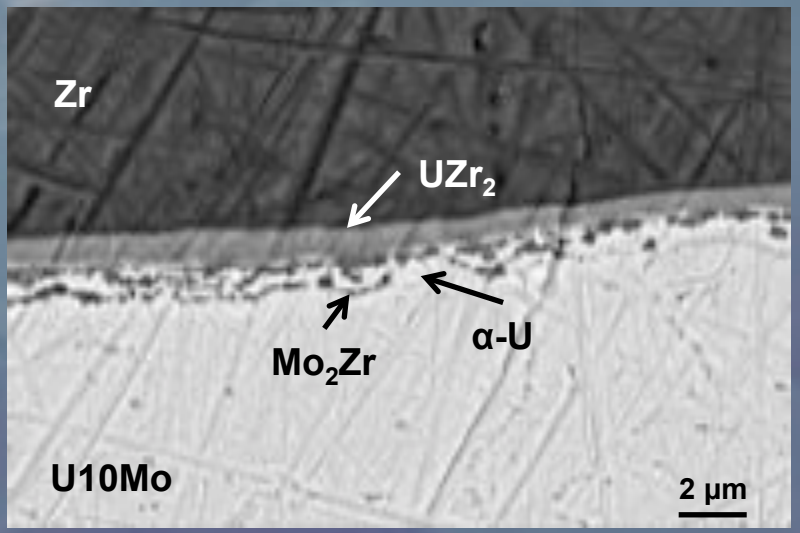
Diffusion Barrier: Zr

Rolled, HIP'ed and Annealed Fuel Assembly







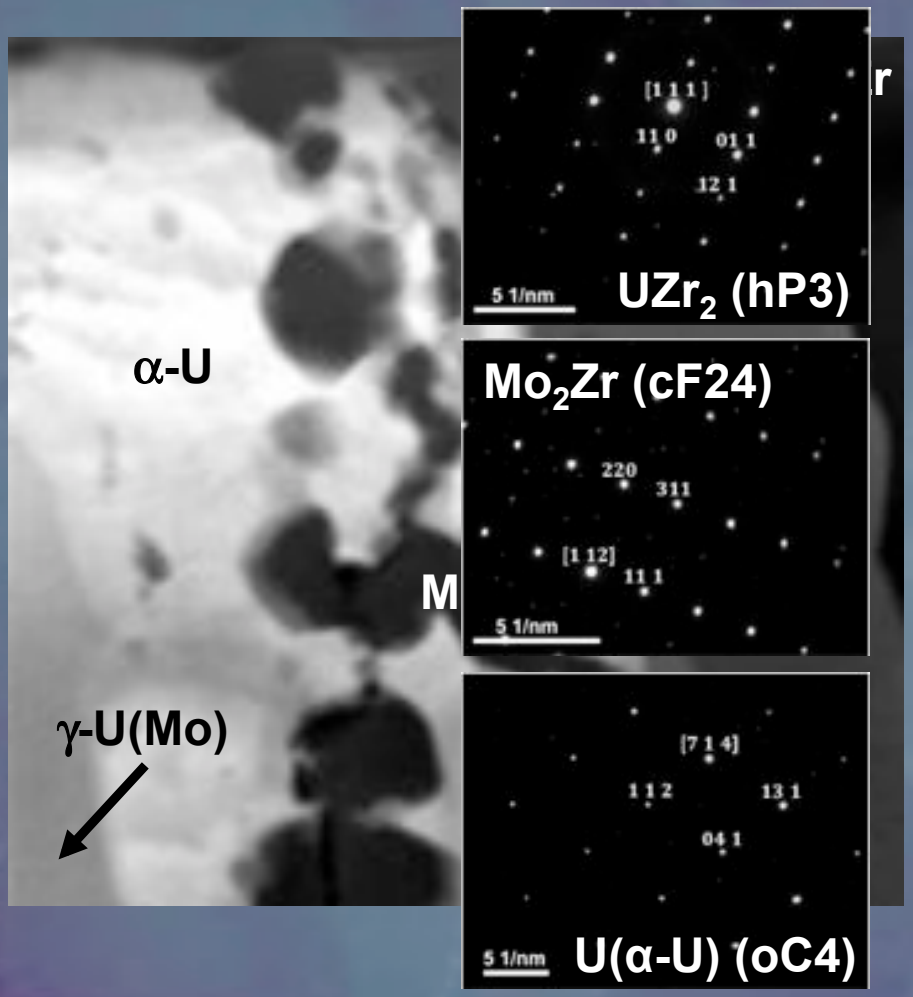


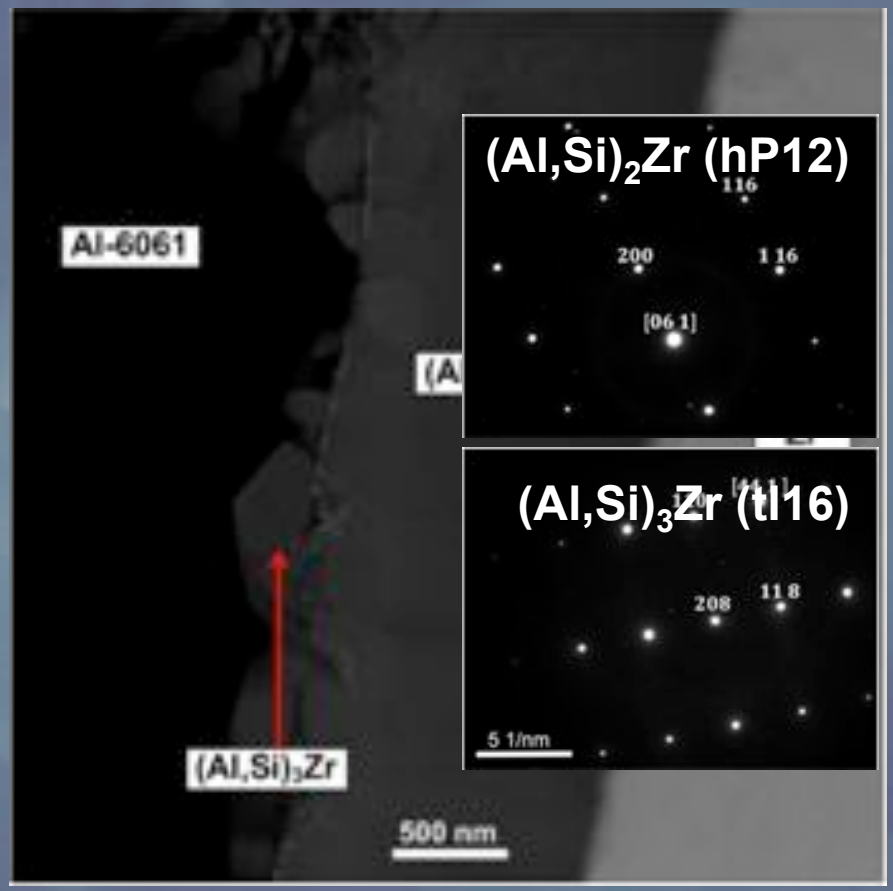
Diffusion Barrier: Zr

Rolled, HIP'ed and Annealed Fuel Assembly

U-Mo vs. Zr Interface

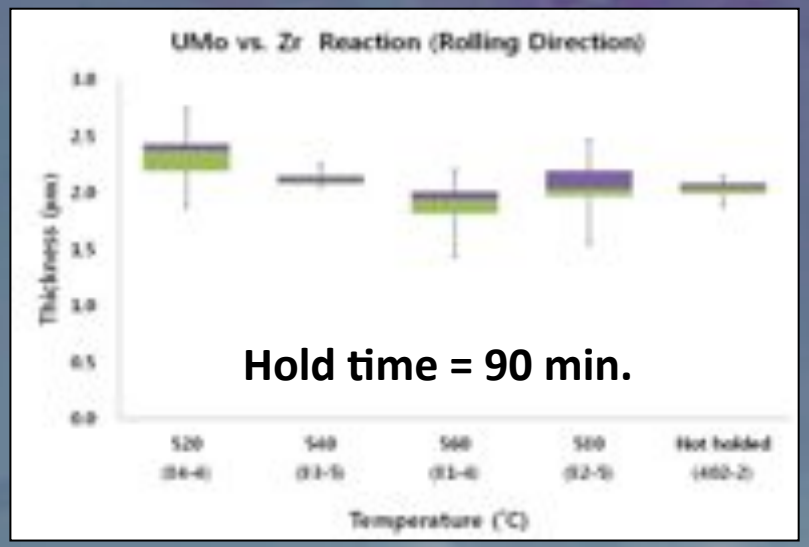
6061 vs. Zr Interface

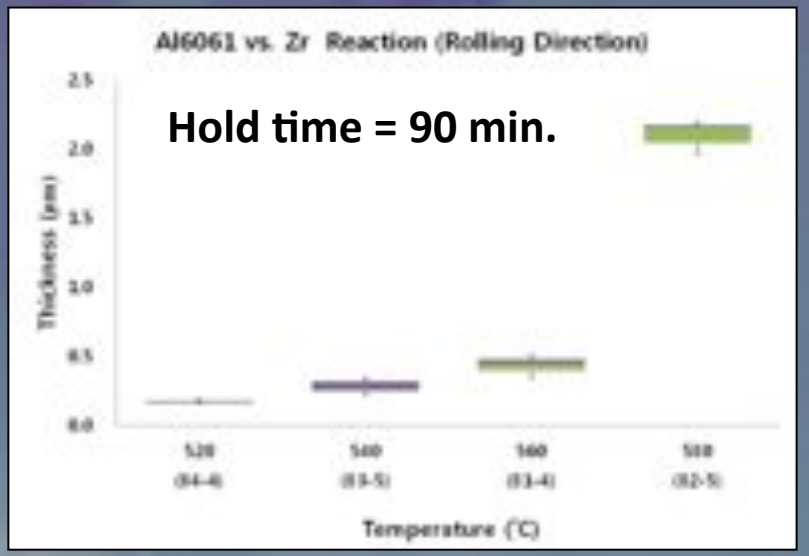


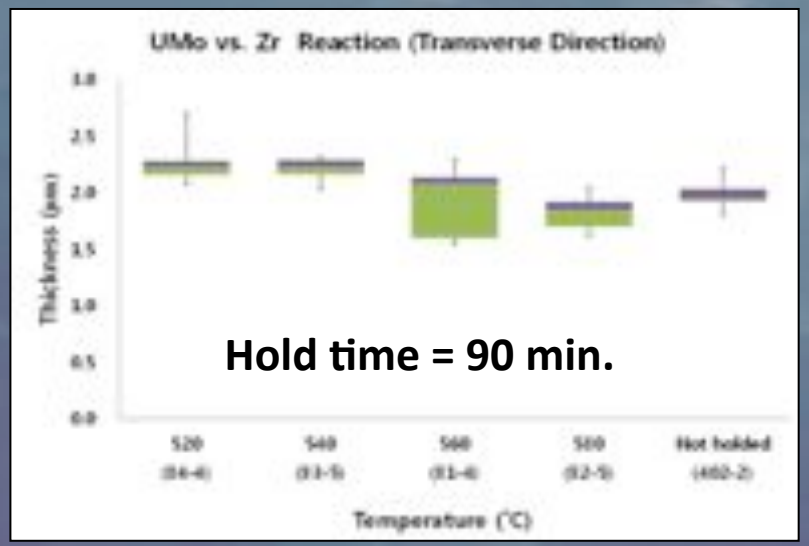


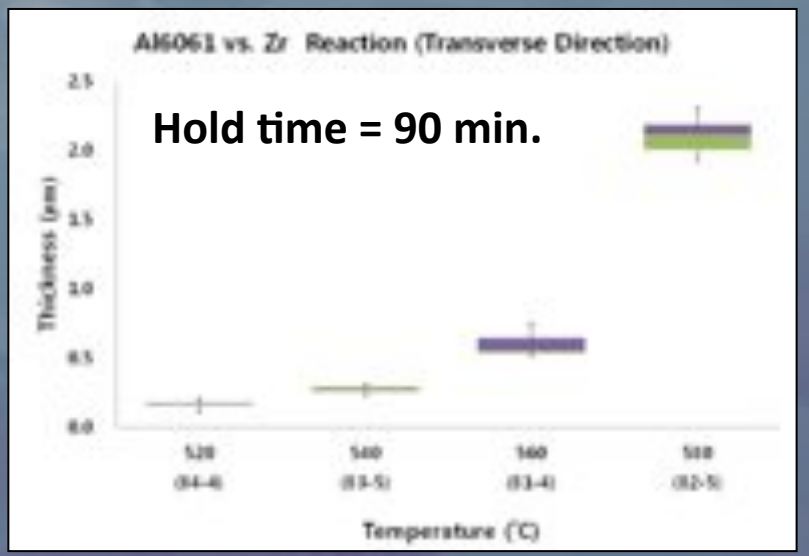
Diffusion Barrier: Zr

Rolled, HIP'ed and Annealed Fuel Assembly



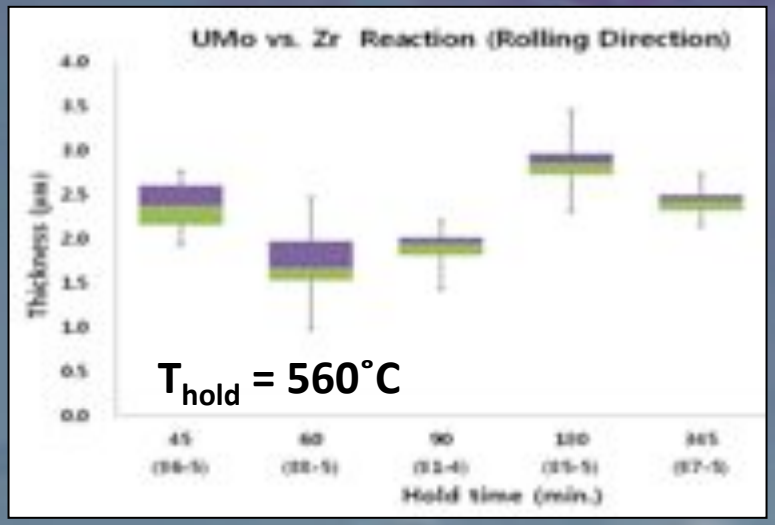


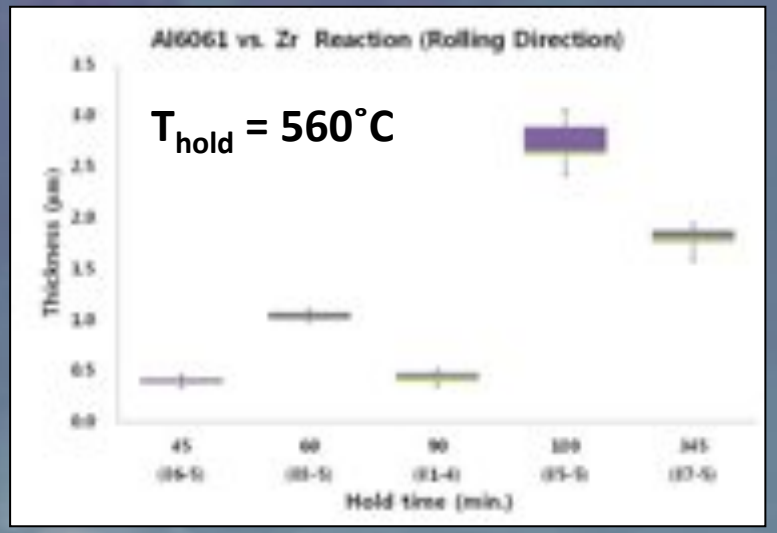


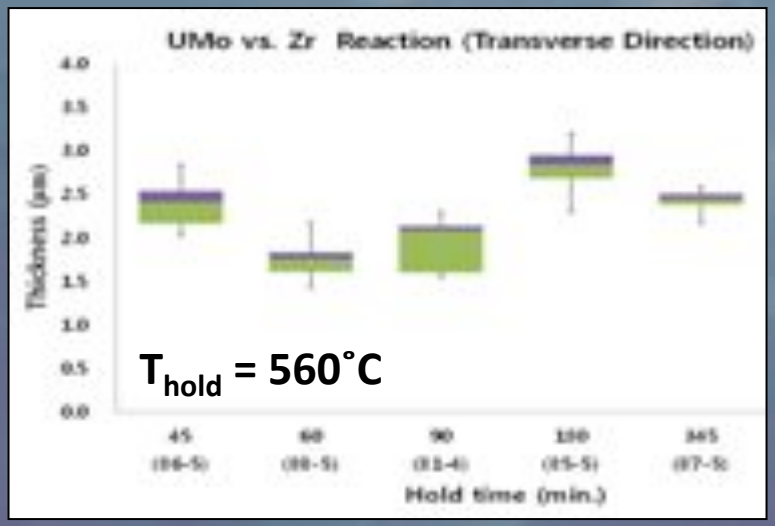


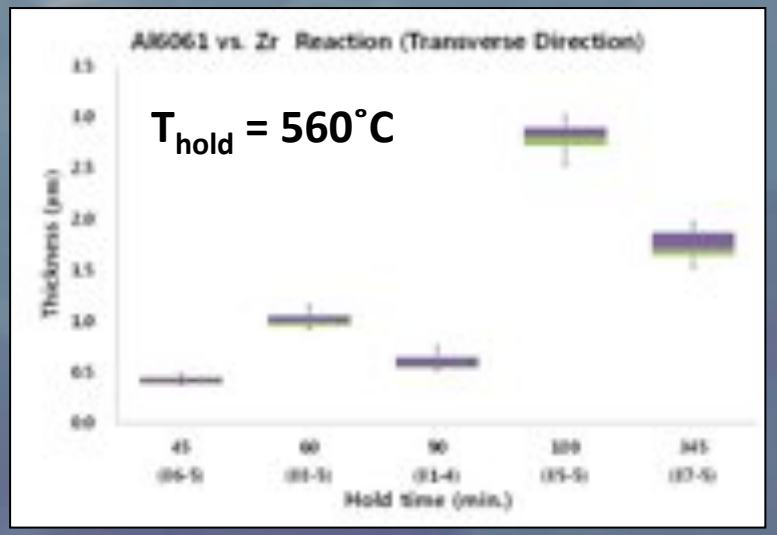
Diffusion Barrier: Zr

Rolled, HIP'ed and Annealed Fuel Assembly



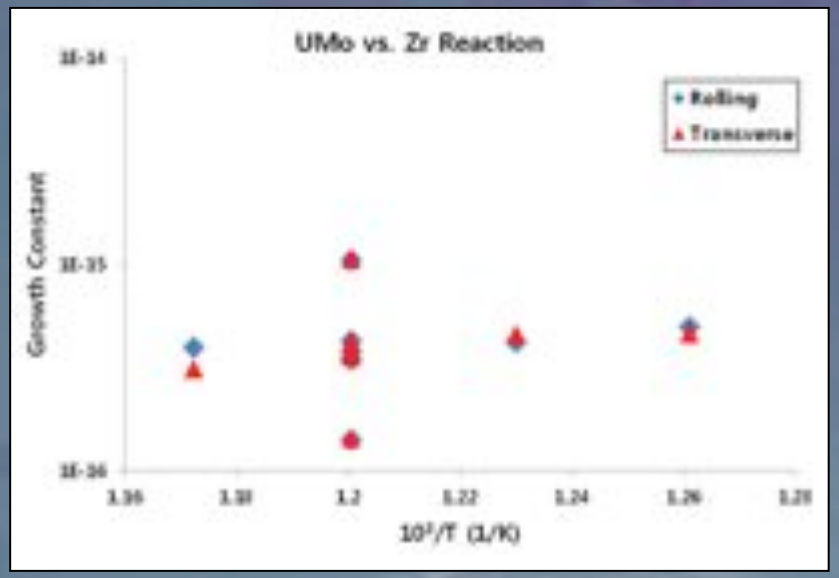


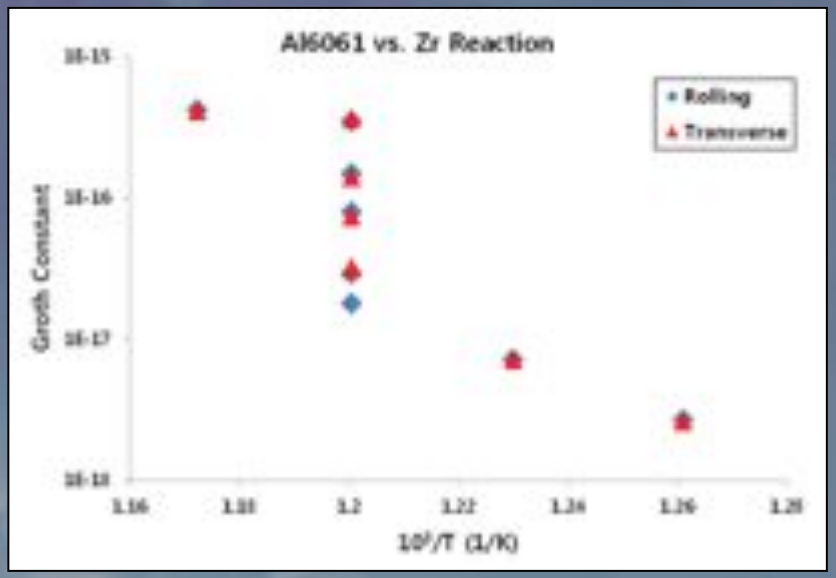




Diffusion Barrier: Zr

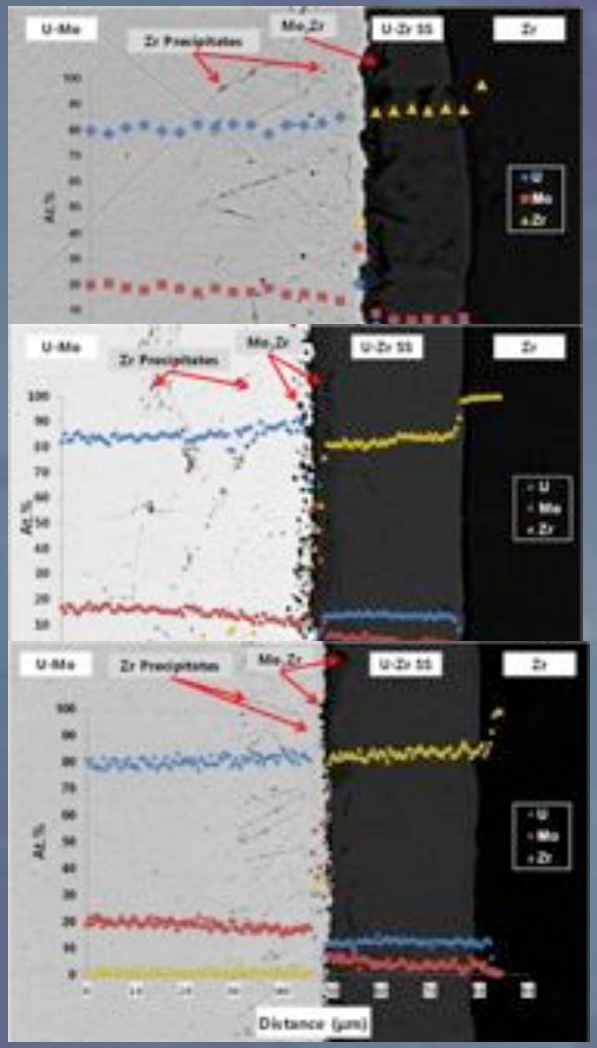
Rolled, HIP'ed and Annealed Fuel Assembly

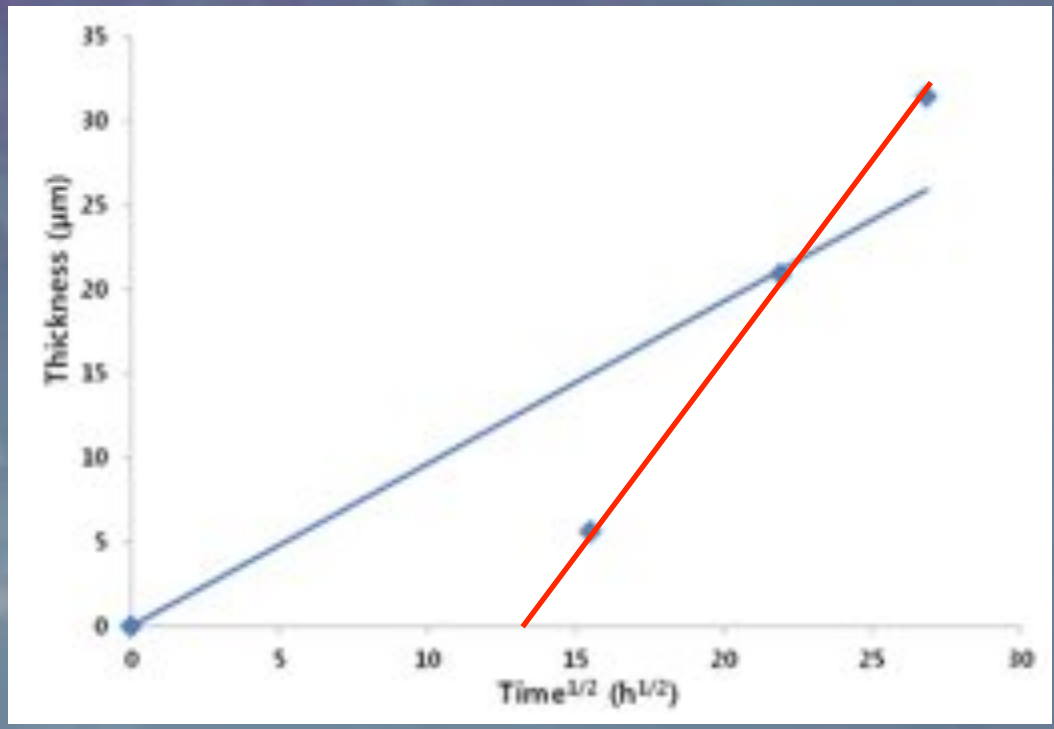




- Negligible diffusional interaction for U-Mo / Zr interface during HIP – most interactions occur during rolling process (650°C).
- Arrhenius temperature dependence for 6061 / Zr Interface - Rolling: 473.30 kJ/mol and Transverse: 473.83 kJ/mol.

Diffusion Barrier: Zr
Time Dependent Interaction at 650°C

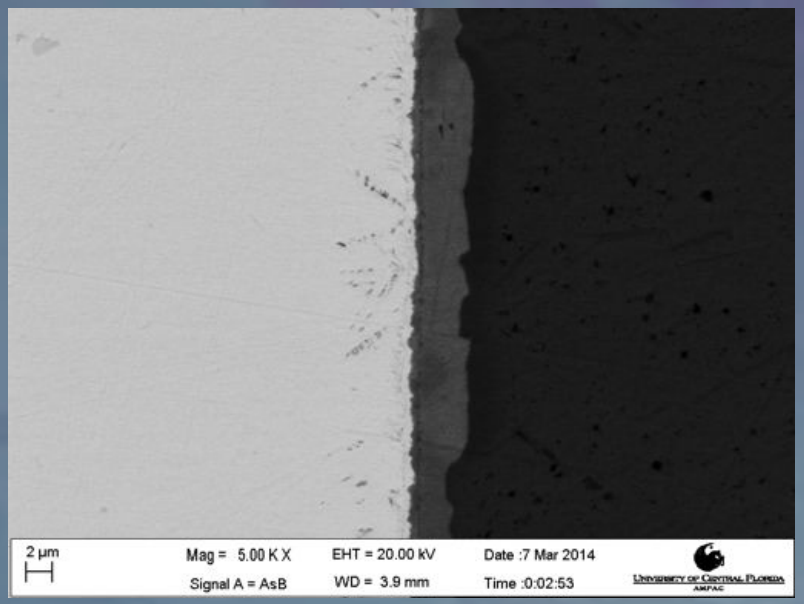


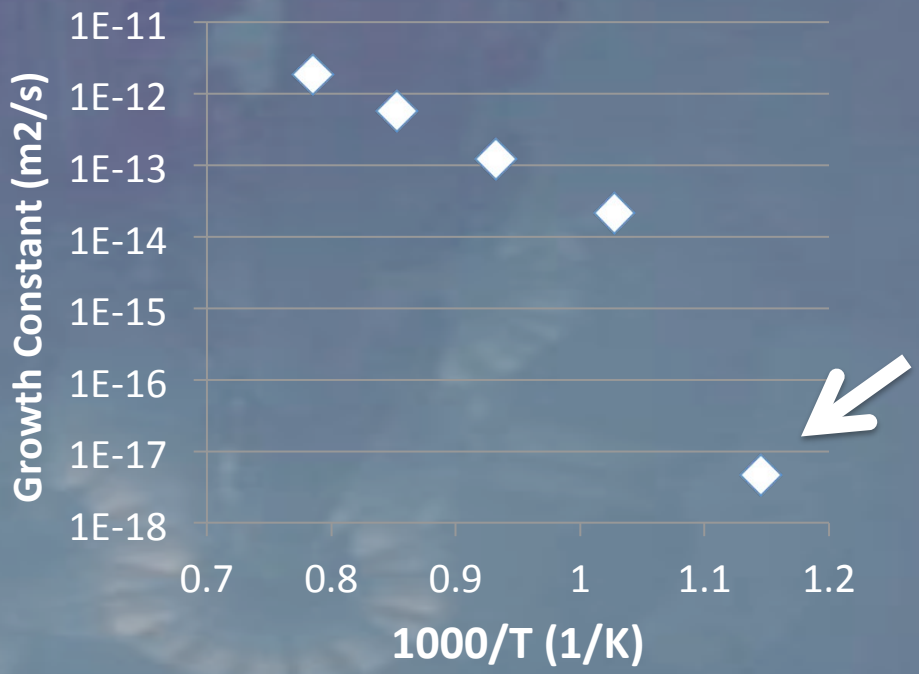


- ✓ Consistent observation of phase constituents and microstructure.
- ✓ Non-parabolic growth rate or incubation period (?).

Diffusion Barrier: Zr

Negligible Interaction at 600°C (960 hrs)





- On-going study on U-Mo-Zr diffusional interactions at lower temperature (650°C to 520°C) as a function of time.

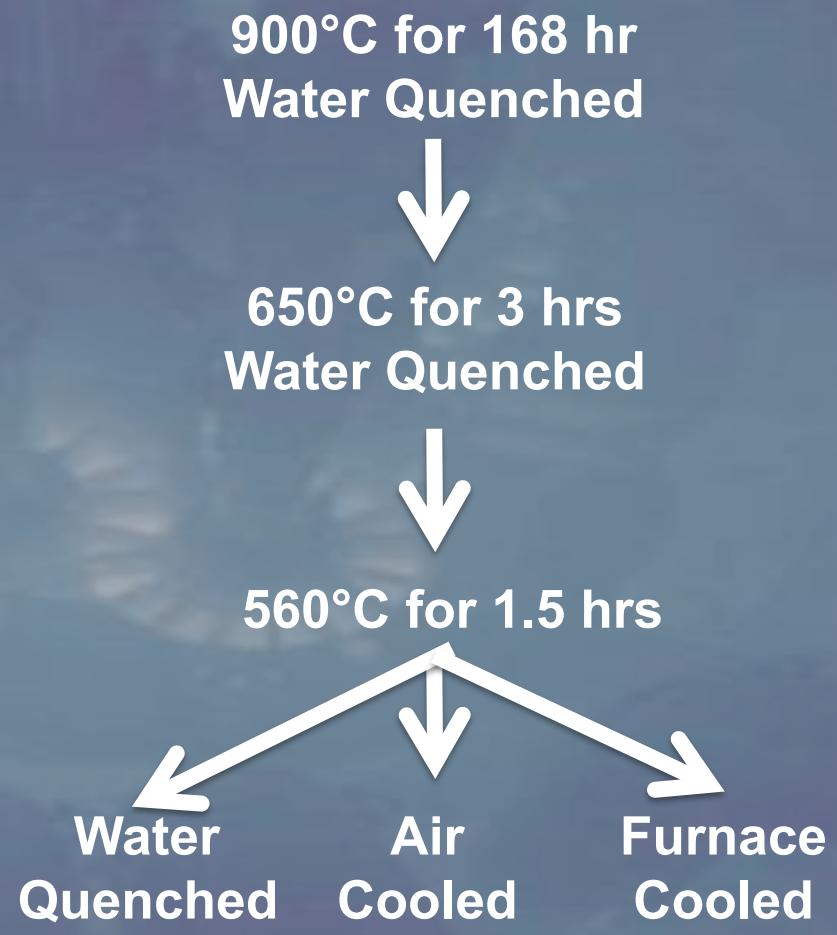
Diffusion Barrier: Zr
Phase Equilibria of U-Mo-Zr

Alloys

U-10Mo
U-10Mo-0.5Zr
U-10Mo-1Zr
U-10Mo-2Zr
U-10Mo-5Zr
U-10Mo-10Zr
U-10Mo-20Zr

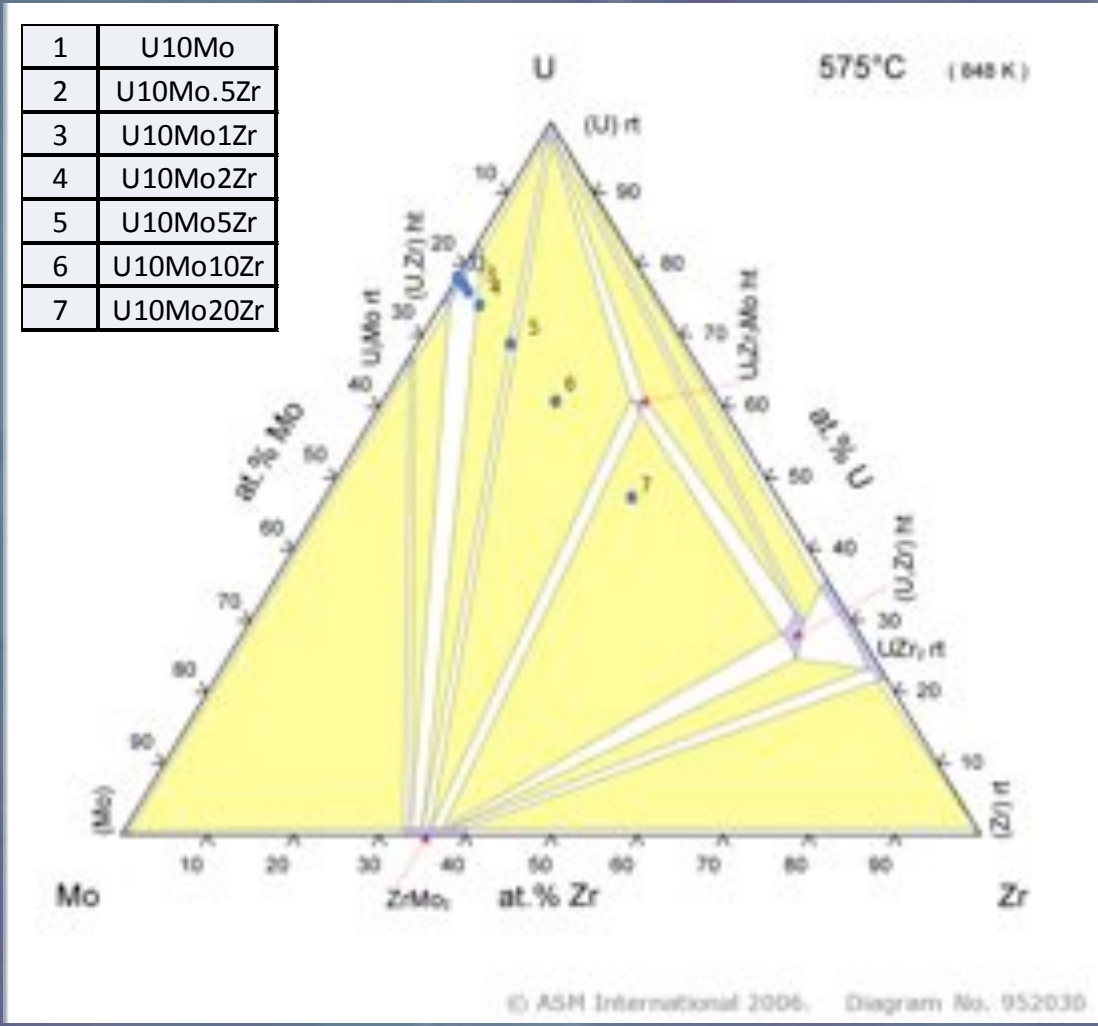
Quantitative Analyses

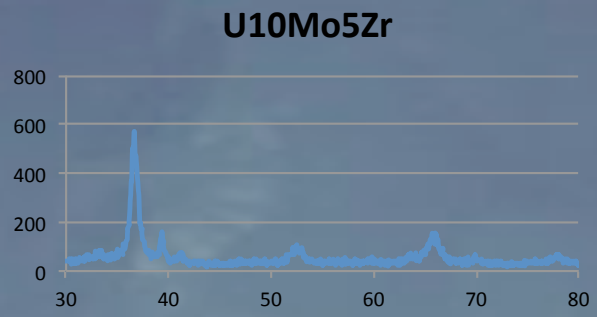
XRD, SEM-Image Analysis

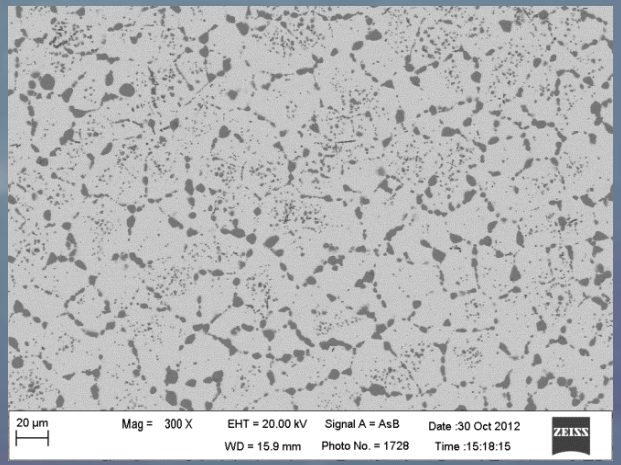


Diffusion Barrier: Zr
Phase Equilibria of U-Mo-Zr

1	U10Mo
2	U10Mo.5Zr
3	U10Mo1Zr
4	U10Mo2Zr
5	U10Mo5Zr
6	U10Mo10Zr
7	U10Mo20Zr

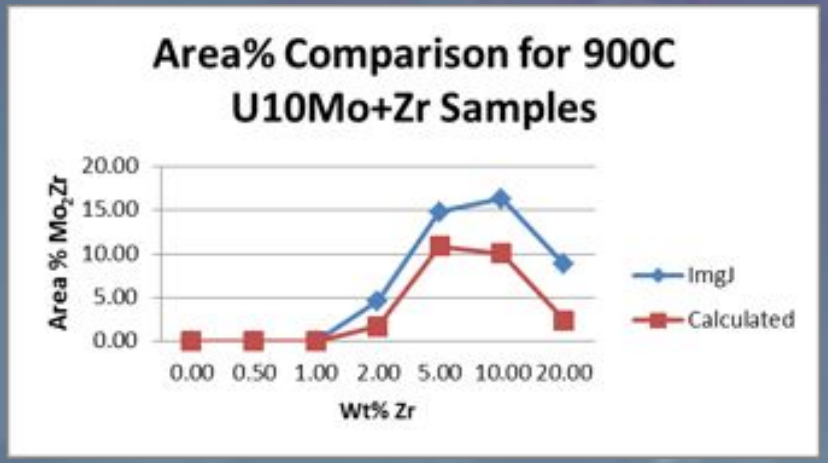


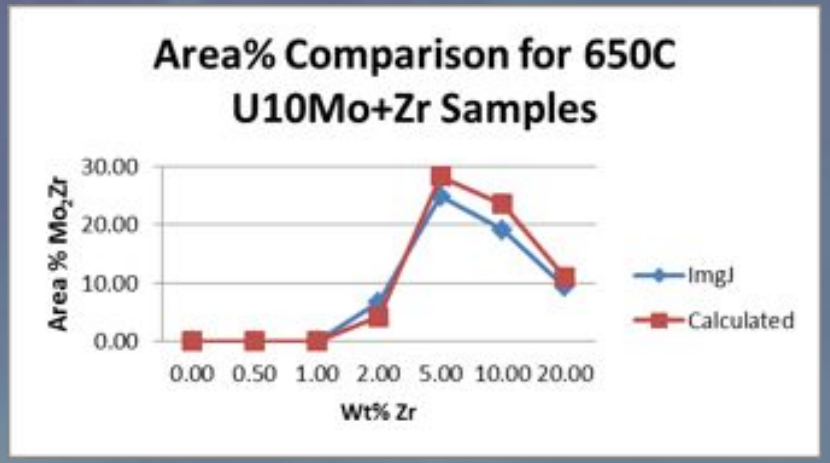


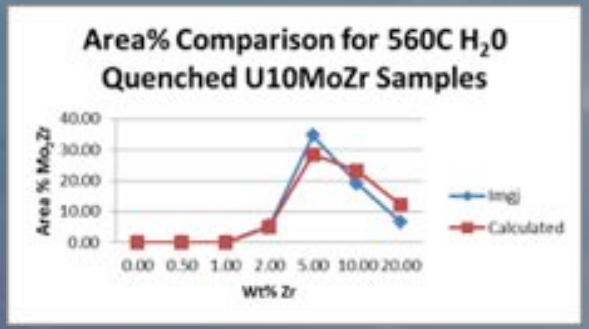


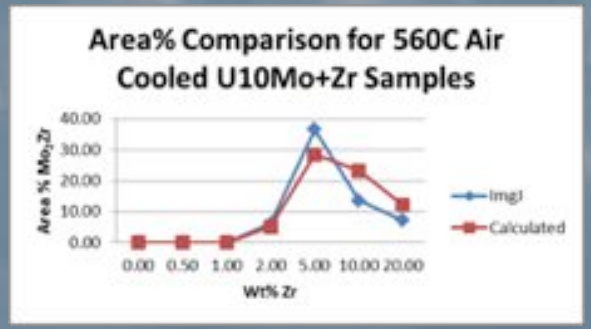
Diffusion Barrier: Zr

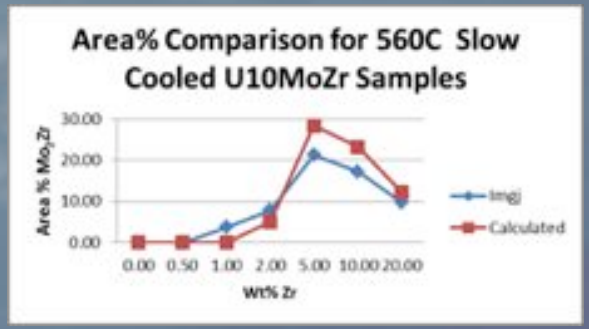
Phase Equilibria of U-Mo-Zr and Cooling Rate







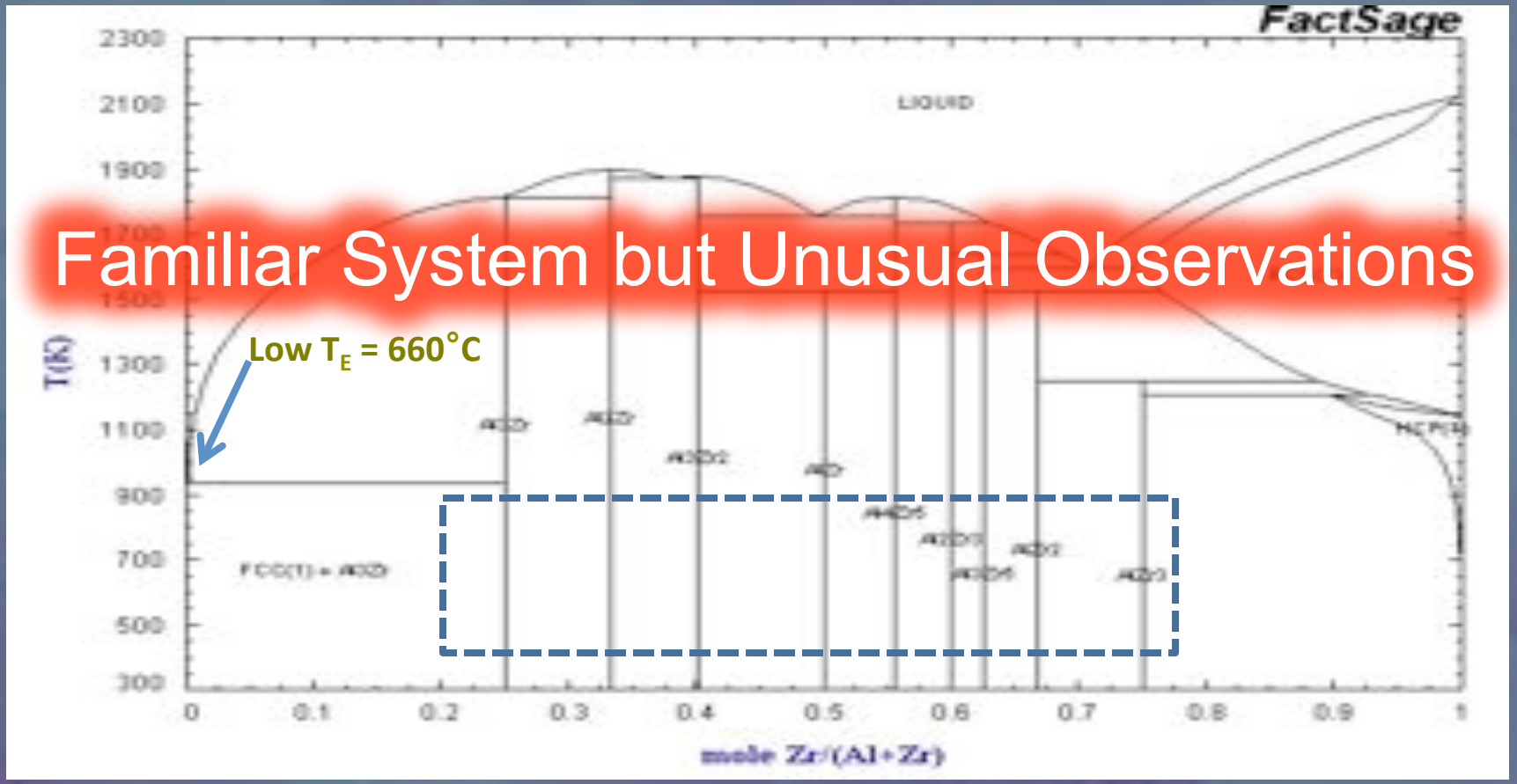




- Generally in good agreement with equilibrium phase diagrams at respective high temperature.

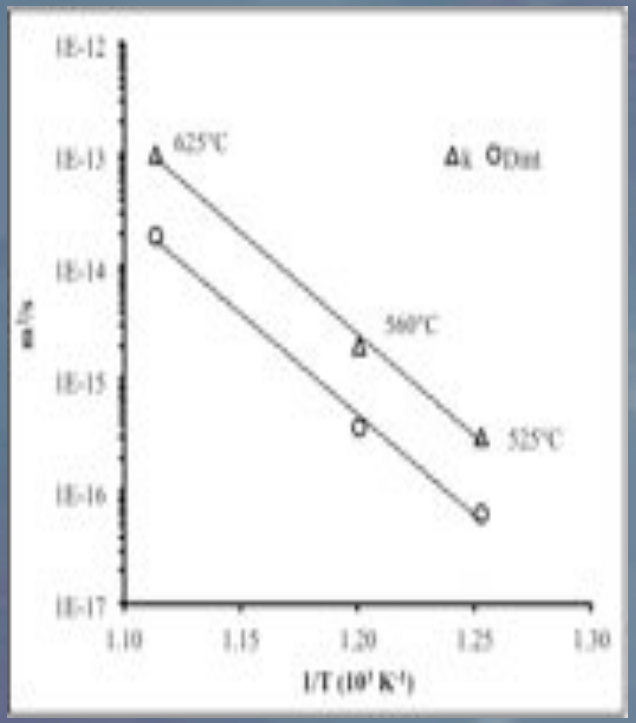
Diffusion Barrier: Zr
Zr vs. Al Alloys Diffusion Couples

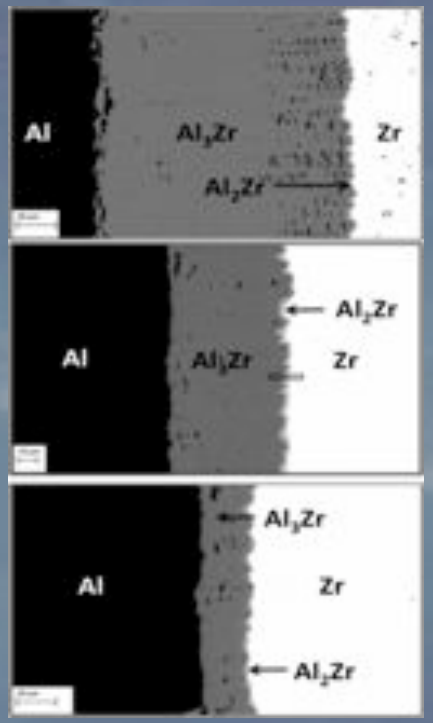
The binary phase diagram indicates the formation of many possible intermetallics in the temperature range of interest.

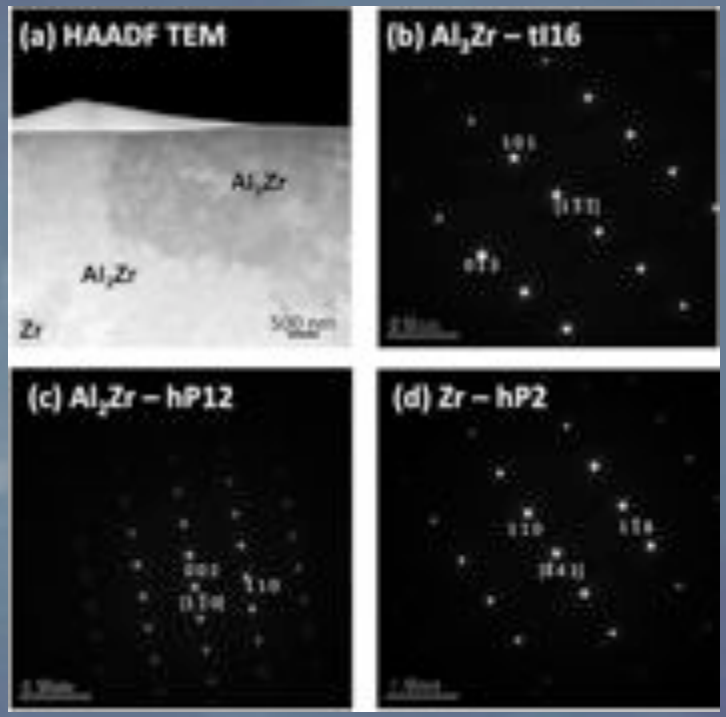


Diffusion Barrier: Zr
Zr vs. Al Alloys Diffusion Couples

Excellent agreement with previously reported (e.g., Kidson, 1964; Laik, 2004) kinetics at temperature above 525°C.

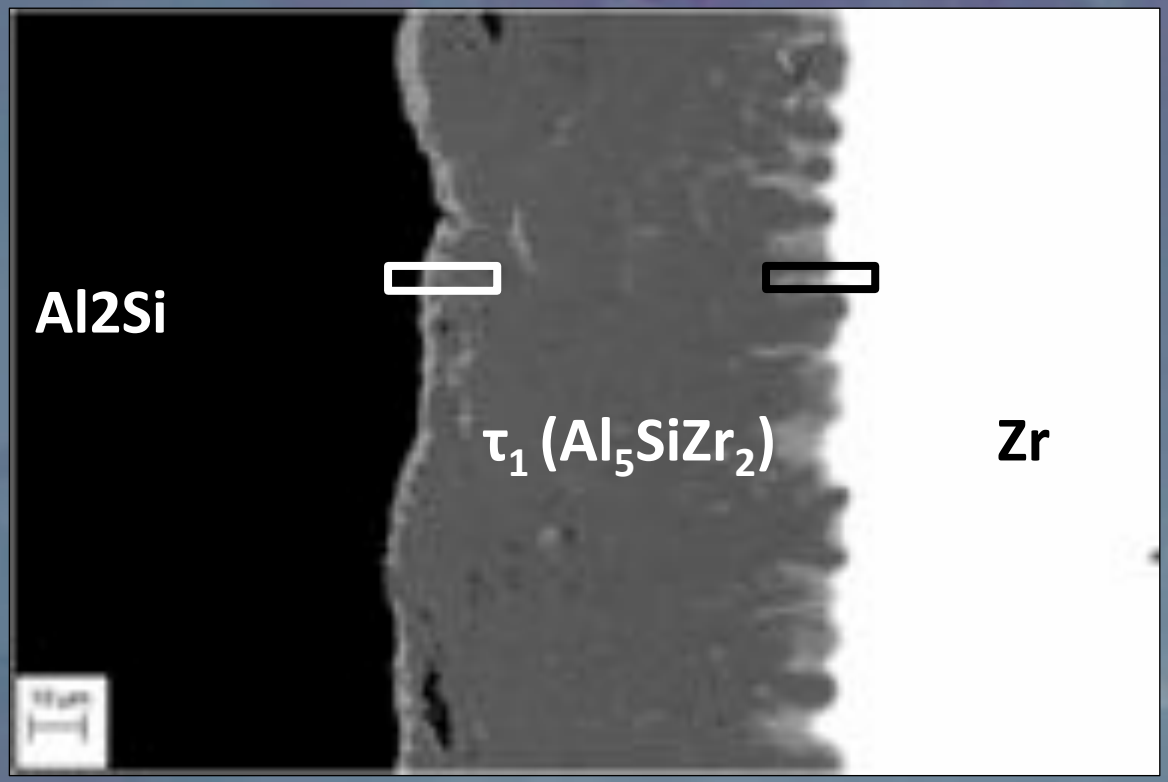


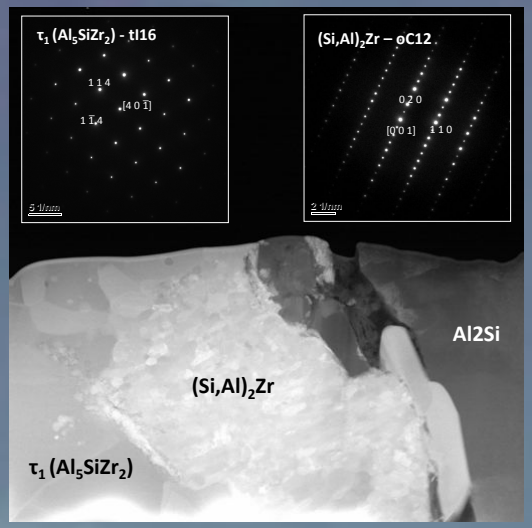


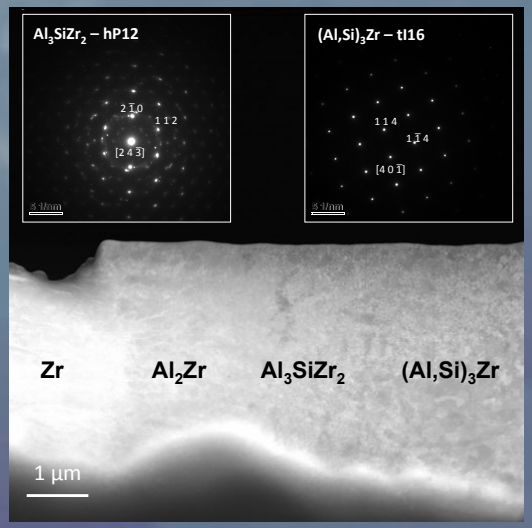


*J. Dickson et al., *Intermetallics*, 2014; 49: 154.

Diffusion Barrier: Zr
Zr vs. Al Alloys Diffusion Couples



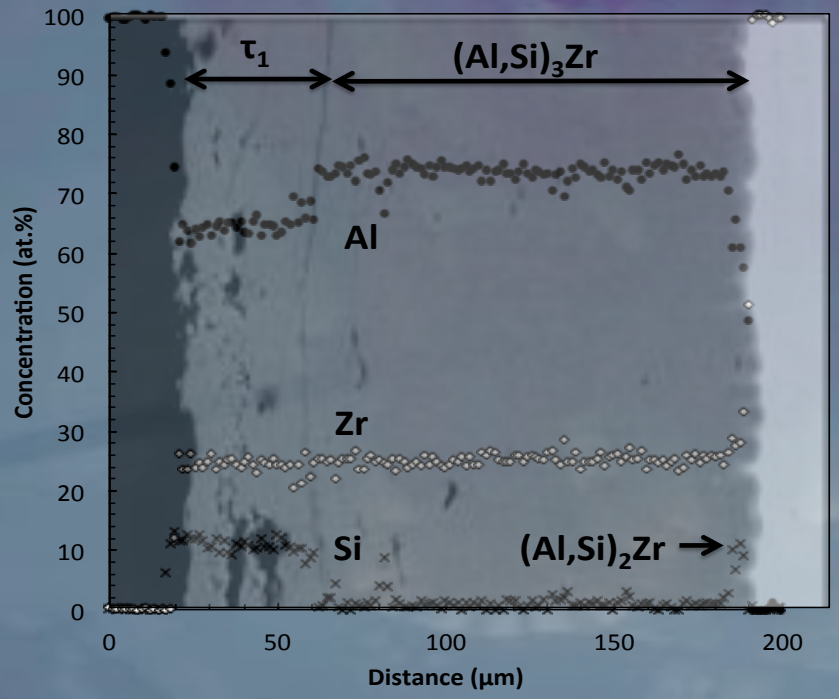


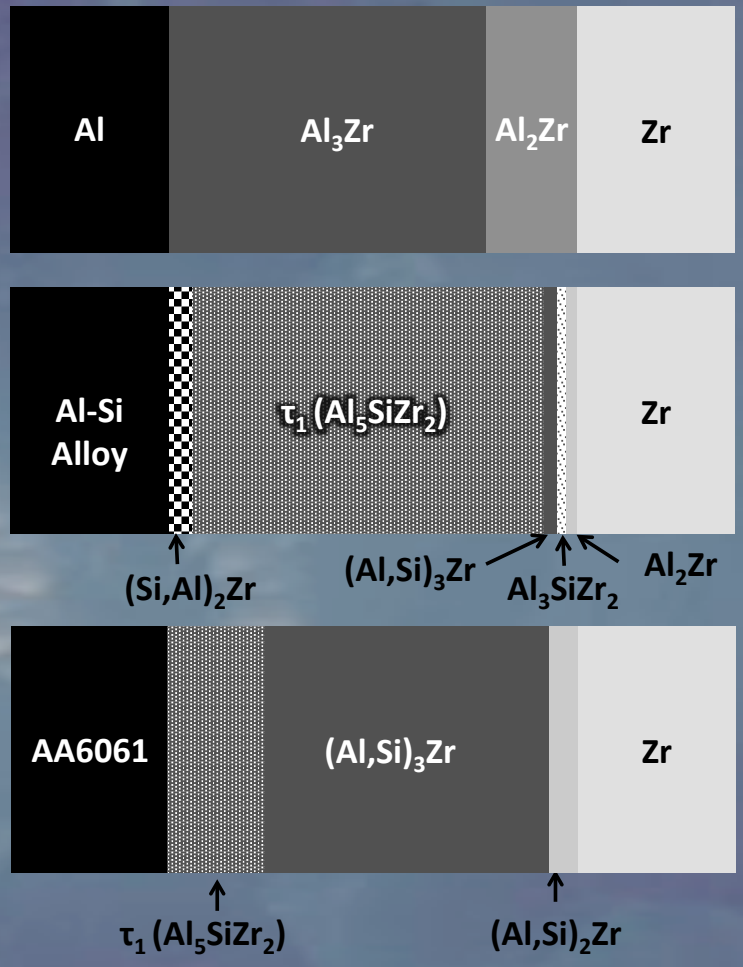


- ✓ Formation and growth of τ_1 (Al_5SiZr_2) ternary intermetallic phase.
- ✓ Similar for Al5Si Alloy.

*J. Dickson et al., *Intermetallics*, 2014; 49: 154.

Diffusion Barrier: Zr
Zr vs. Al Alloys Diffusion Couples



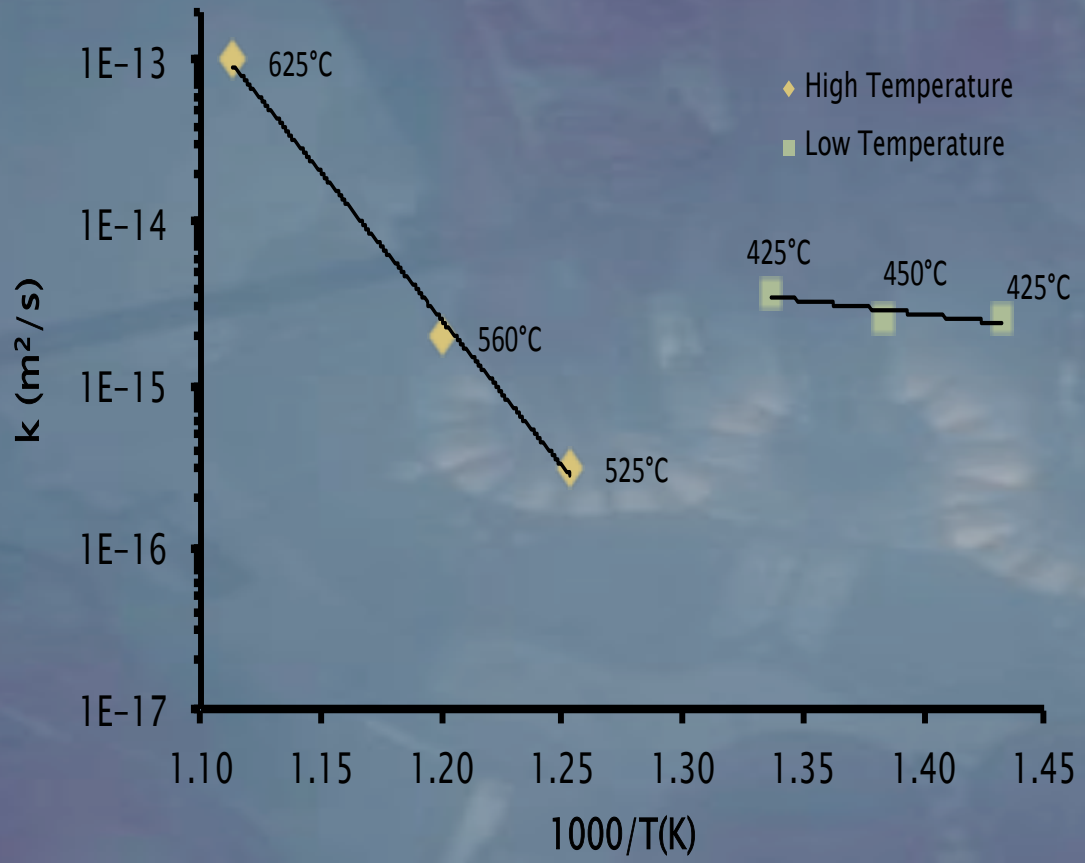


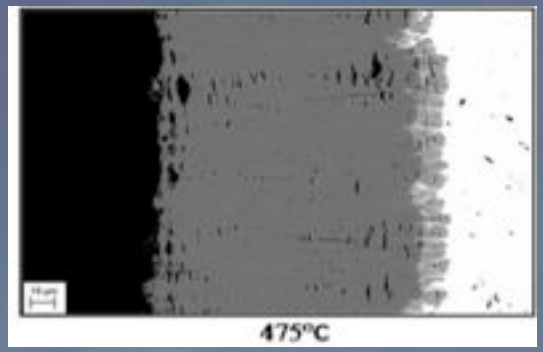
- ✓ Formation and growth of both τ_1 (Al_5SiZr_2) ternary intermetallic and binary $(Al,Si)_3Zr$ phases.
- ✓ Distinguished by Si content.

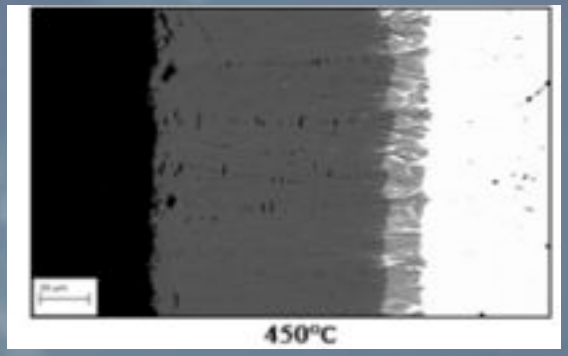
*J. Dickson et al., *Intermetallics*, 2014; 49: 154.

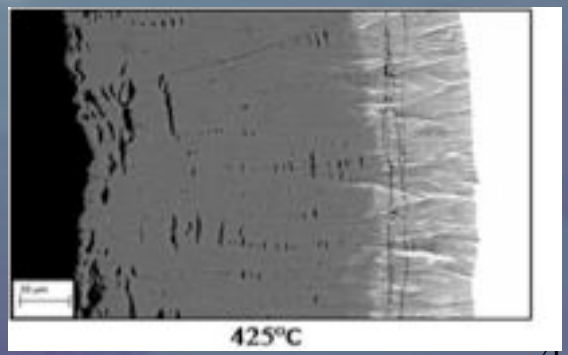
Diffusion Barrier: Zr
Zr vs. Al Alloys Diffusion Couples

Unusual behavior at lower temperature.









Dickson et al., Unpublished Research.

RERTR: Summary

1. For U-Mo vs. Al diffusion couples, the interdiffusion zones in diffusion couples U-Mo vs. pure Al annealed at 550˚ and 600˚C consisted of finely distributed UAl_3, UAl_4, $U_6Mo_4Al_{43}$ and UMo_2Al_{20} phases in stratified microstructures.

2. For U-Mo vs. Al-Si diffusion couples, fast diffusing Si and Al result in the development of the $(U,Mo)(Al,Si)_3$ and UMo_2Al_{20} phases. The UAl_4 and $U_6Mo_4Al_{43}$ (potentially with poor irradiation behavior) phases do "not" develop in the interdiffusion zone. Addition of Si decreases the growth rate of interaction zone.

3. Zr, Mo, Nb and Mg barriers were examined for interaction kinetics with U-Mo alloy; all exhibited significant reduction in the rate of interaction by few to several orders of magnitude.

RERTR: Summary

4. Rolled, HIP'ed and annealed fuel plate samples are being examined for phase constituents and interdiffusion/reaction kinetics as functions of temperature and time.

5. U-Mo-Zr phase equilibria as a function of temperature and quench is being investigated – preliminary results indicate that phase constituents generally agree with respective high temperature.

6. Detailed interdiffusion and reaction mechanisms, including those at lower temperature, are being investigated for interaction between Zr and Al alloys.

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